THE SYNTHESES AND CHARACTERIZATION OF BINUCLEAR CLATHROCHELATE COMPLEXES

Thesis by

William Alan Marritt

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ABSTRACT

A series of binuclear clathrochelate complexes, $M_A(II)M_B(II)L^+$, have been synthesized and characterized for the purpose of examining electrostatic, magnetic, and electronic delocalization effects in binuclear complexes. The clathrochelating ligand, L^{3-}, is a bicyclic Schiff-base compound derived from 3 equiv of 2-hydroxy-5-methylisophthalaldehyde and 2 equiv of 2, 2′, 2″-triaminotriethylamine (tren). The following $M_A(II)M_B(II)L^+$ complexes were prepared by combinations of metal-ion template, metathesis, and insertion reactions: homonuclear complexes with $M_A = M_B$ = Mn, Fe, Co, Cu, Zn, and Cd; heteronuclear complexes with M_A = Mn, M_B = Co, Ni, Zn, Cd, and Mg; M_A = Fe, M_B = Mn, Co, Ni, Cu, Zn, Cd, and Mg; M_A = Cu, M_B = Mn, Co, Ni, Zn, Cd, and Mg. In addition, syntheses and characterization are reported for the binuclear $Cu(II)Cu(II)LH^{2+}$ complex and mononuclear complexes of the non-deprotonated ligand, MLH_3^{n+}, with M = Na(I), Mn(II), Mn(III), Fe(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Mg(II).

The M_A redox potentials of the Mn(III)/Mn(II), Fe(III)/Fe(II), and Cu(II)/Cu(I) couples were determined by cyclic voltammetry and differential pulse voltammetry for three series containing both homonuclear and heteronuclear complexes, $Mn(II)M_B(II)L^+$, $Fe(II)M_B(II)L^+$, and $Cu(II)M_B(II)L^+$. Within experimental error, the average of the M_A redox potentials for each series of heteronuclear complexes was the same as that for the corresponding homonuclear complex. This result suggests that there is no measurable stabilization of $Mn(III)Mn(II)L^{2+}$, $Fe(III)Fe(II)L^{2+}$, and Cu(I)Cu(II)L with respect to mixed-valent heteronuclear analogues.

The magnetic properties of a series of four homonuclear $M_A(II)M_B(II)L^+$ complexes were examined by variable temperature susceptibility measurements ($M_A = M_B$ = Mn, Fe, Co, and Cu). In all cases, weak antiferromagnetic coupling between the metal centers was observed ($-33.5\ cm^{-1} < J < -0.8\ cm^{-1}$). The weakness is attributed to limited overlap of metal orbitals with those of the bridging atoms.

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CHAPTER 1

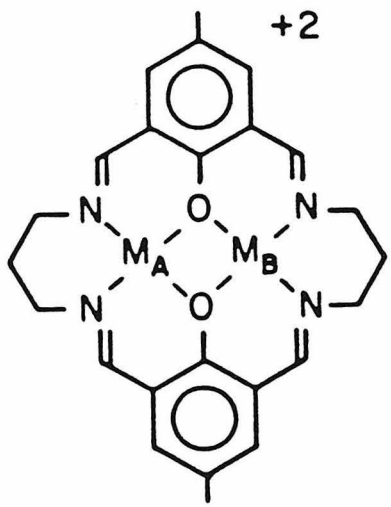
Introduction

Many of the most interesting, primary enzymatic processes involve multinuclear metal centers.[1,2] Processes such as substrate binding, substrate activation, and electron transfer often require the presence of two or more active metals to supplement the bioorganic "backbone" of the enzyme. Indeed, arguments can be made that the major role of the organic portion of the protein in enzymes such as cytochrome c oxidase, a metalloprotein with two iron and two copper centers,[2] is to position and rigidly hold the metal ions in the appropriate interacting environment that is required for the proper functioning of the enzyme. In this respect, one of the major challenges of modern synthetic inorganic chemistry is to prepare simple models of the enzyme's active metal sites which mimic the behavior of the metalloproteins. At a more fundamental level, many research groups are preparing systems containing two or more metal atoms in structurally well defined environments to study the nature of basic metal-metal interactions. An understanding of these processes, such as electrostatic interactions, magnetic interactions, and electronic delocalization between metals is essential to elucidating mechanisms of the more complex phenomena of enzyme action.

An understanding of these metal-metal interactions has equally important applications for non-enzymatic systems. For example, multimetal systems are used in industrially important catalytic reactions,[3] in some fuel-cell electrode materials,[4] and in artificial photosynthetic devices used for solar energy conversion.[5] A typical example of the first system is the bismuth-molybdate conglomerate which is used in the SOHIO process for the catalytic ammoxidation of

propylene to acrylonitrile.[6] Co-facial bimetallic porphyrin systems show some promise as possible fuel-cell electrode components for the electrocatalytic reduction of O_2 to H_2O.[7] Typical examples of the third system include colloidal $RuO_2/Pt/TiO_2$ particles[8] and molybdenum-halogen clusters.[9]

A few multimetallic systems yielding information relating to the fundamental nature of intermetallic interactions have been particularly well studied. Foremost among these systems are the ruthenium dimer complexes which have been examined extensively by Taube,[10] Meyer,[11] and Sutin,[12] among others. These systems have provided considerable information on electronic delocalization phenomena for mixed-valent states. Another well studied system of this type includes complexes of type 1. These studies have addressed the nature of both magnetic



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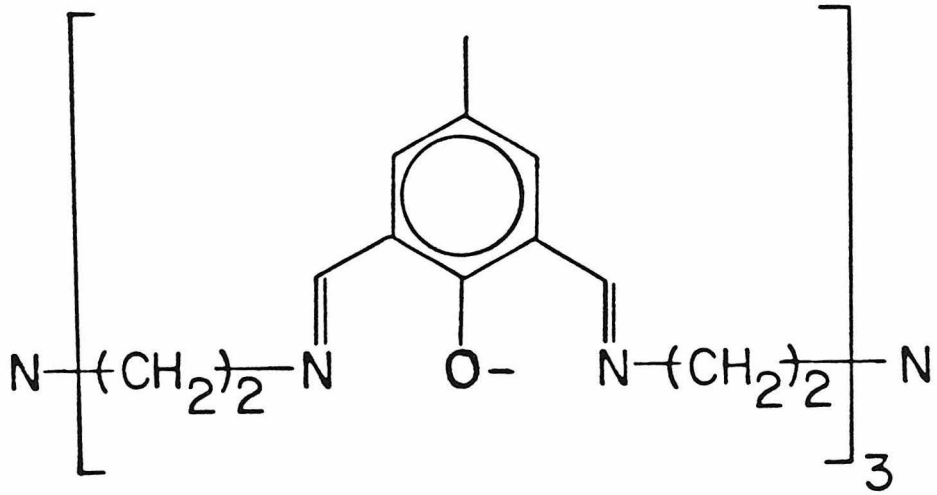
interactions[13] and electronic delocalization.[14] A final example, systems containing two or more iron atoms studied by Ludi[15] and Brown,[16] show electronic delocalization similar to the ruthenium dimers

mentioned previously. However, since iron is a common enzymatically active metal[17] (in contrast to ruthenium) the results from these systems have added significance in light of their biological applicability.

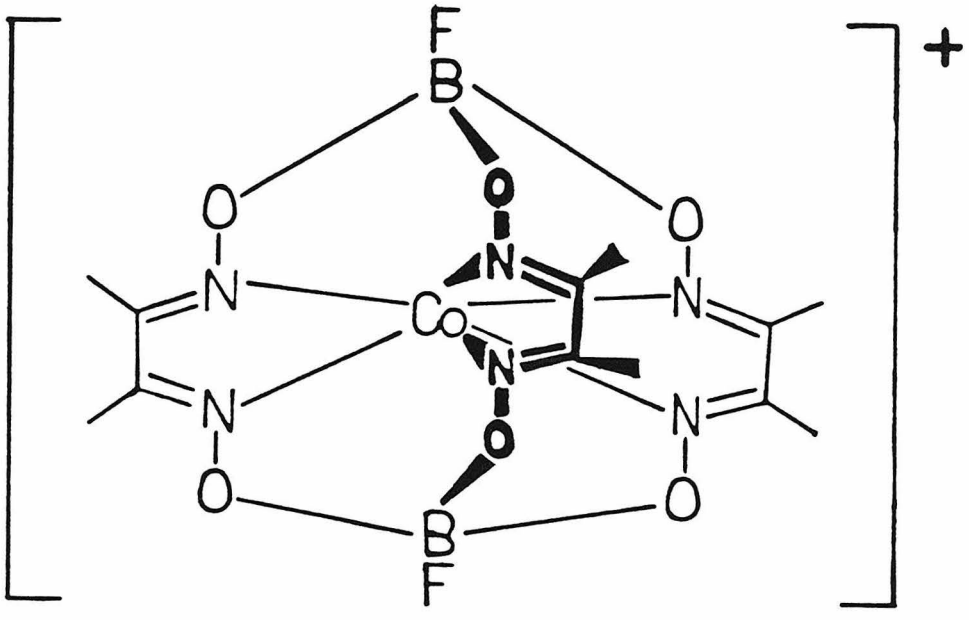
Our approach towards understanding metal-metal interactions in a well-defined ligand environment entailed the preparation of binuclear complexes of the ligand, L^{3-}, and examination of their properties by electrochemical and magnetic techniques. Complexes of this type in



L^{3-}

which metal ions are completely encapsulated by a rigid polydentate ligand are known as clathrochelates. Such complexes were first described and named in 1964 by Busch;[18] however, an example was not forthcoming until 1968.[19] Since there are relatively few examples of these clathrochelate complexes, a brief comprehensive review is given below.

The first example, 2, reported by Rose, is a mononuclear Co(III) complex prepared by the reaction of $Co(dimethylglyoxime)_3^{3+}$ and BF_3.[20]



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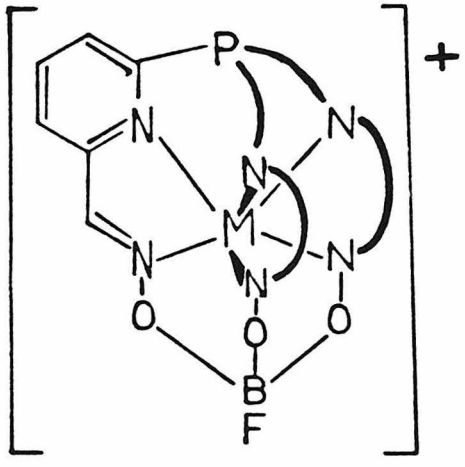
This reaction method, addition of a Lewis acid to alkoxy substituents, proved to be useful for the preparation of related clathrochelates.[21]

Holm and co-workers prepared a series of the mononuclear clathrochelates (3) by a multistep synthesis using Rose's Lewis acid addition in the last step.[22] X-ray structural studies for a series of



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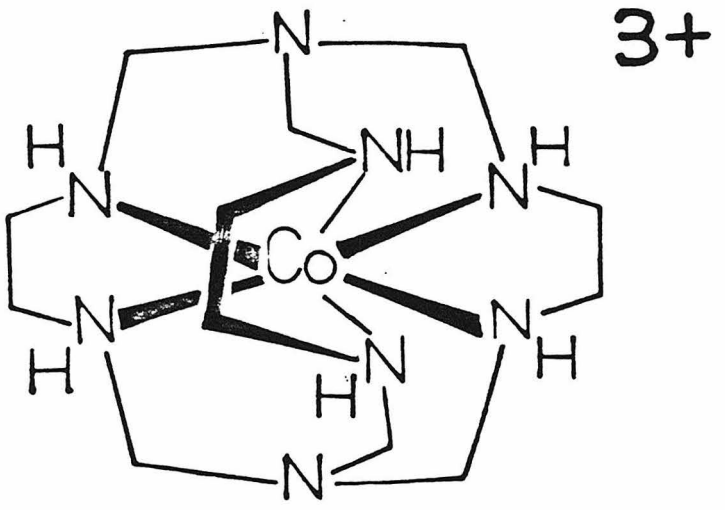
these complexes provided useful information for correlating metal-ion electronic configuration with the metal's preference for trigonal prismatic vs. trigonal antiprismatic coordination geometry.

Sargeson and co-workers have prepared several mononuclear clathrochelates incorporating a bicyclic octaamine ligand which they have dubbed sepulchrates (4).[23] The Co(III) complex is prepared from



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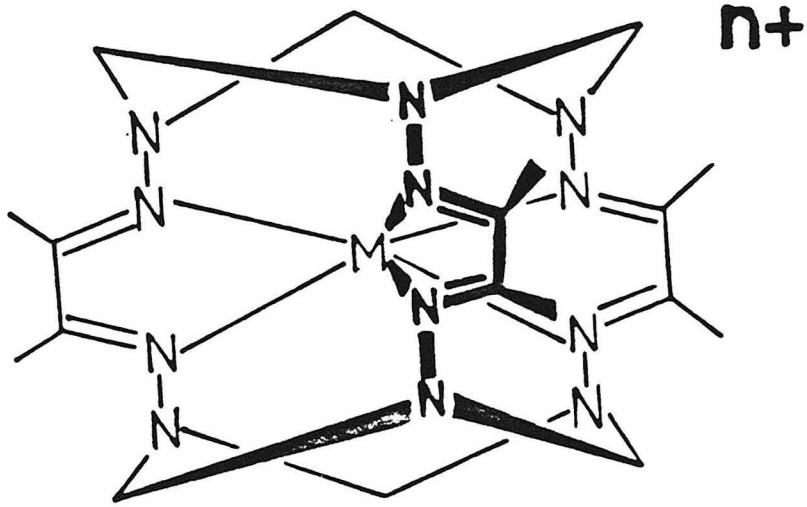
the reaction of Co(ethylenediamine)$_3^{3+}$ with ammonia and formaldehyde. This particular complex has found application in electron-transfer studies with the ligand remaining fully associated with the metal ion in the normally substitution-labile +2 oxidation state.[24]

In the course of studies of planar, macrocyclic Ni(II) complexes, Goedken and co-workers isolated mononuclear clathrochelates (5) as minor byproducts.[25] The synthesis of these clathrochelates has since been improved and generalized for metal ions other than Ni(II).[26]



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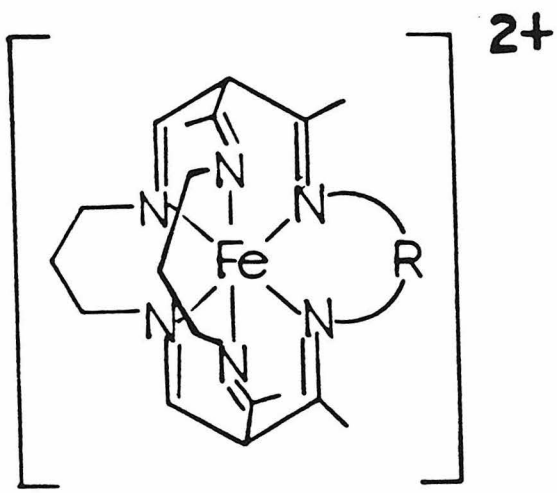
In a recent report, Busch and co-workers detail the syntheses and characterization of a new family of clathrochelates (6).[27] A unique



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aspect of this system is that these complexes are prepared by a base-

induced rearrangement of an originally tetradentate complex. Additionally, the authors suggest the possibility that this rearrangement reaction might be chemically reversible.

The new clathrochelates of L^{3-} described herein are unique with respect to the other known clathrochelates in that they include two metal ions within a rigid ligand environment. Syntheses and characterization of both homonuclear and heteronuclear complexes of L^{3-} are presented in Chapter 2. In addition, electrochemical studies of these complexes are reported and the results are discussed in terms of their relationship to metal-metal interactions. In Chapter 3, a variable temperature magnetic study for a series of these complexes is detailed. This work was done in collaboration with Professor D. N. Hendrickson and Mark Timken at the University of Illinois. Additionally, the syntheses and characterization of several mononuclear and binuclear complexes of 1,3-bis(2-pyridylimino)isoindoline ligands are described in Appendices 1 and 2.

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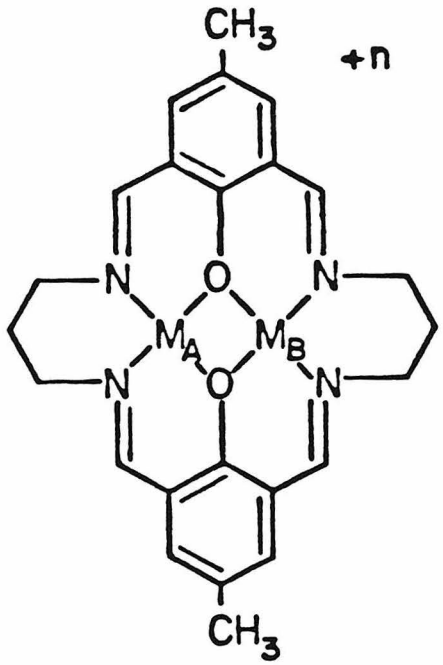
CHAPTER 2

The Syntheses and Electrochemical Properties of Binuclear Clathrochelates

INTRODUCTION

Binuclear complexes of type 1 have been studied by electrochemical,[1,2] magnetic,[3-5] and spectroscopic[2,6] methods. These studies have been aimed at understanding the nature of interactions



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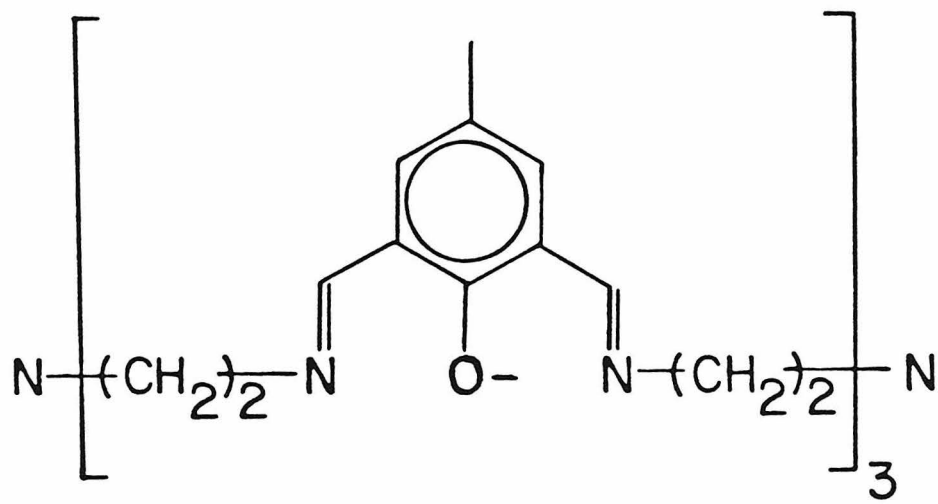
between metal ions.

One general approach towards studying metal-metal interactions in complexes of type 1 is to examine physical, chemical, and/or redox properties of these complexes while varying the metal ions systematically.[1,3-5] Differences in the measured properties are attributed to variations in metal-metal interactions, if it can be established that metal-ligand geometry is nearly identical for the series examined. In an electrochemical study of type 1 complexes with M_A = Cu(II) and M_B = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II), there is evidence

which suggests that structural differences as a function of these M_B ions are minimal. However, since axial-ligand geometry cannot be rigorously controlled in type $\underset{\wedge}{1}$ complexes, structural variations dependent on the nature of both metal ions are certainly possible. Indeed, there is structural evidence for differing axial-ligand geometries for several type $\underset{\wedge}{1}$ complexes.[7-9]

Our approach towards examining metal-metal interactions in binuclear complexes was to prepare complexes related to those of type $\underset{\wedge}{1}$ for which metal-ligand geometries are likely to be less variable. The ligand which was chosen for this purpose, L^{3-}, is a bicyclic Schiff-base compound derived from 3 equiv of 2-hydroxy-5-methylisophthaldehyde and 2 equiv of 2,2′,2″-triaminotriethylamine (tren). The term

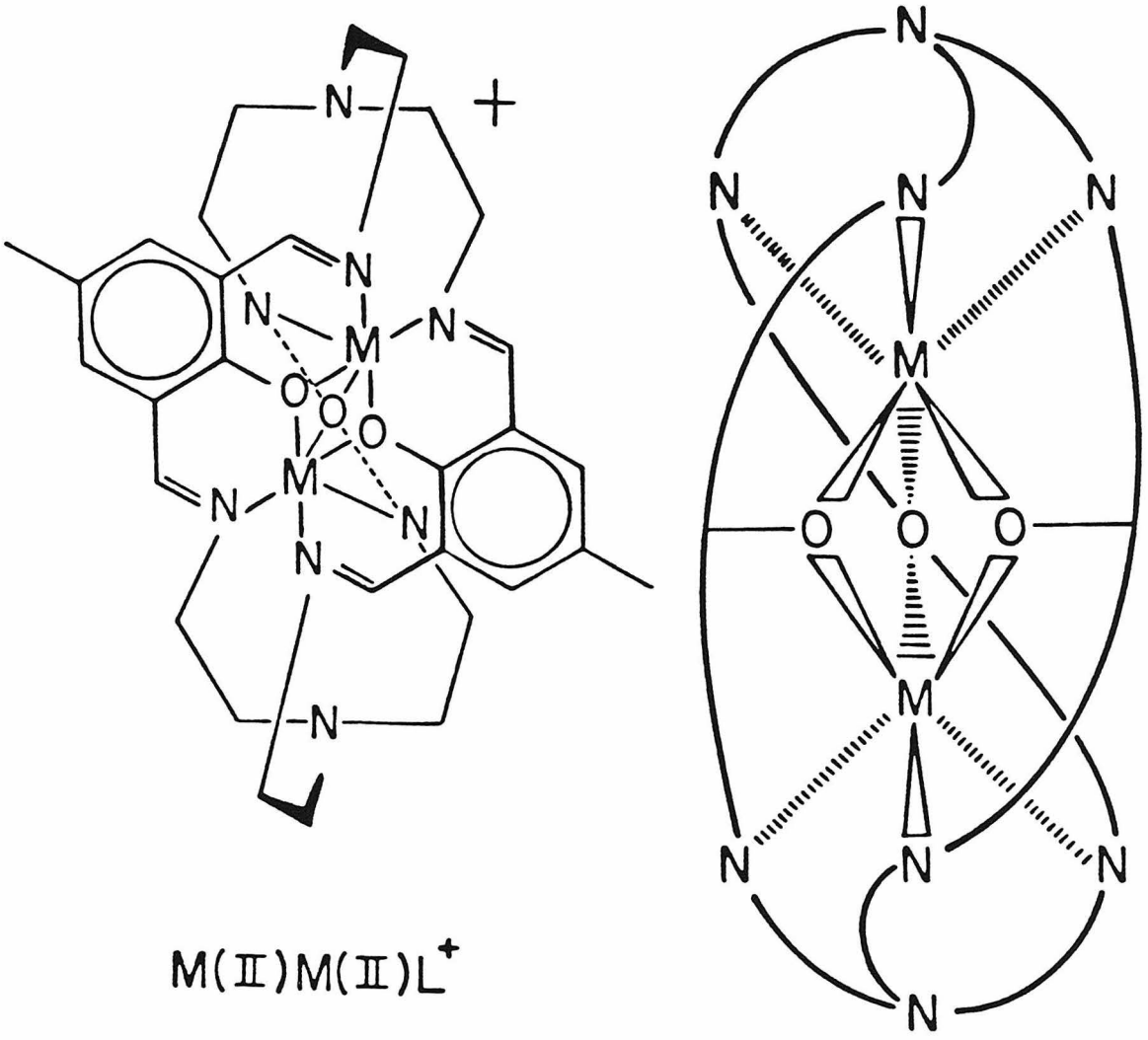


$\underset{\sim}{L^{3-}}$

clathrochelate has been used to describe complexes of ligands such as L^{3-} in which the metal ions are totally encapsulated by a ligand.[10]

Two conceptual illustrations of binuclear M(II) clathrochelates of this ligand are shown in Figures 1a and 1b. Based on structural studies of mononuclear complexes with remotely similar ligands,[11] the geometry for each metal ion in binuclear clathrochelates of L^{3-} is expected to be nearly trigonal antiprismatic[12,13] (see Figure 1b). Since clathrochelating ligands have limited structural freedom, it was expected that metal-ligand geometries of $M(II)M(II)L^{+}$ complexes would not vary significantly as a function of the metal ions.

The synthesis, characterization, and electrochemical properties of $M(II)M(II)L^{+}$ complexes are reported here. Also included is a discussion of the differences between the electrochemical behavior of $M(II)M(II)L^{+}$ complexes and that of type $\underset{\sim}{1}$ complexes with M_A = Cu(II) and M_B = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II). Additionally, synthesis and characterization of mononuclear complexes of the non-deprotonated ligand, LH_3, are reported.

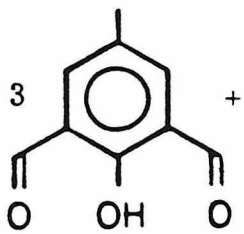


(a) (b)

Figure 1. Illustrations of M(II)M(II)L^+ showing (a) the chemical structure (the dotted line represents the third 2-hydroxy-5-methylisophthaldehyde fragment) and (b) the expected trigonal antiprismatic geometrical structure.

RESULTS

Synthesis. Binuclear complexes of the clathrochelating ligand L^{3-} were first prepared by a metal-template reaction. Condensation reactions of 3 equiv of 2-hydroxy-5-methylisophthalaldehyde and 2 equiv of tren, in the presence of certain metal (II) salts and base, yielded cationic binuclear complexes, $M(II)M(II)L^{+}$ (eq 1). Thus far

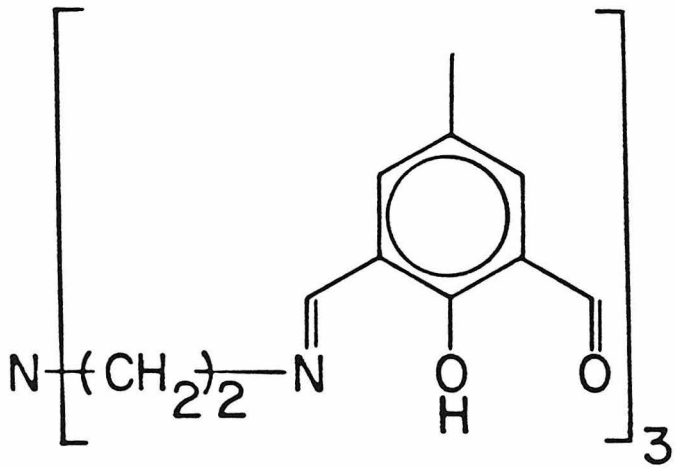


$$+ 2\ \text{tren} + 2\ M(II) \xrightarrow{\text{base}} M(II)M(II)L^{+} \qquad M(II) = \text{Mn and Cd} \qquad (1)$$

the success of this method has been limited to Cd(II) and Mn(II) salts. Intractable mixtures, which probably contain polymeric Schiff-base compounds, were obtained from similar reactions using salts of Cr(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II). The binuclear Cd(II) complex, $Cd(II)Cd(II)L^{+}$ has been isolated as NO_3^-, BPh_4^-, ClO_4^-, PF_6^-, and BF_4^- salts. Only the BF_4^- salt is appreciably soluble in solvents such as acetonitrile, N,N-dimethylformamide (DMF), dimethylsulfoxide, and methylene chloride. For this reason, $Mn(II)Mn(II)L^{+}$ and related binuclear complexes, prepared by alternate methods (vide infra), were isolated as BF_4^- slats.

For the preparation of $M(II)M(II)L^{+}$ complexes with metals other

than Cd(II) and Mn(II), it was necessary to devise synthetic strategies other than the one-step template synthesis. A multistep synthesis has been developed by which both binuclear and monomuclear clathrochelate complexes have been prepared. The primary step is the preparation of the Schiff base 2 derived from 1 equiv of tren and 3 equiv of 2-hydroxy-



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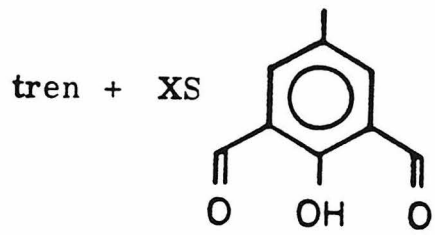
5-methylisophthalaldehyde. A difficulty in preparing 2 is the high probability for the multifunctional reactants to form Schiff-base condensation polymers instead of 2. It is likely, for this reason, that several attempts to prepare 2 by methods reported for related Schiff bases[14] yielded intractable mixtures. The polymerization problem was circumvented, however, and 2 has been isolated in high yield by reacting tren with excess 2-hydroxy-5-methylisophthalaldehyde under conditions which favor the rapid crystallization of 2 (eq 2).

The second step in this multistep synthesis is the formation of mononuclear clathrochelate complexes using template reactions of 2 with both tren and a metal salt. Several template reactions were screened after initial attempts to prepare the free ligand, LH_3, from



(2)

high dilution reactions of tren and 2 failed to yield identifiable products. We found that mononuclear complexes in which the ligand is not deprotonated, $M(II)LH_3(BF_4)_2 \cdot H_2O$, were isolable from reactions of 2 with 1 equiv of tren and 1 equiv of certain metal(II) salts (eq 3). Thus far

$$2 + \text{tren} + M(II) \rightarrow M(II)LH_3^{2+} \qquad (3)$$

M(II) = Mn, Fe, Co, and Cd

only Mn(II), Fe(II), Co(II), and Cd(II) mononuclear complexes have been prepared by this approach; similar reactions using Cr(II), Ni(II), Cu(II), and Zn(II) salts yielded intractable mixtures.

This template method, although useful, has several drawbacks in addition to being metal-ion specific. First, to obtain material of reasonable purity, the complexes must be slowly crystallized over a period of several days. Second, despite slow crystallization, samples of $M(II)LH_3(BF_4)_2 \cdot H_2O$ frequently contain detectable amounts of the corresponding binuclear complexes, $M(II)M(II)LBF_4 \cdot xH_2O$. Levels of binuclear contamination are highest for the Mn(II) and Co(II) complexes. Third, product yields are relatively low, being less than 50%. For

these reasons, efforts were made to develop alternative synthetic routes to $M(II)LH_3^{2+}$ complexes.

As a result of these efforts, a general synthesis for $M(II)LH_3^{2+}$ complexes has been developed which utilizes an alkali-cation template reaction. Treatment of $\underset{\sim}{2}$ with 1 equiv of both tren and $NaNO_3$ affords the mononuclear complex, $NaLH_3NO_3$, in high yield (eq 4). Yellow

$$\underset{\sim}{2} + \text{tren} + NaNO_3 \rightarrow NaLH_3NO_3 \qquad (4)$$

crystalline material is obtained which is moderately soluble in solvents such as methanol, acetonitrile, and methylene chloride. Based on thermodynamic and kinetic studies of (alkali-cation)-cryptate complexes by J. M. Lehn and co-workers,[15] it seemed reasonable that exchange of divalent metal ions for Na^+ in $NaLH_3NO_3$ would be thermodynamically favored and would occur rapidly. Indeed, upon addition of 1 equiv of a M(II) salt to a methanolic solution containing 1.1 equiv of $NaLH_3NO_3$, the initially orange-yellow solution changes color almost immediately to that characteristic of the divalent metal complex, $M(II)LH_3^{2+}$. By this exchange method (eq 5), $M(II)LH_3^{2+}$ complexes of Mn, Fe, Co, Ni,

$$M(II) + NaLH_3NO_3 \rightarrow M(II)LH_3^{2+} + NaNO_3 \qquad (5)$$

Zn, Cd, and Mg have been prepared and isolated as monohydrated BF_4^- salts. These complexes are soluble in acetonitrile, DMF, and dimethylsulfoxide.

Mononuclear complexes prepared by this method contain insignificant amounts of binuclear contamination. Apparently, for most metal ions, insertion of a second metal ion into $M(II)LH_3^{2+}$ does not

occur as facilely as the initial exchange reaction. For Cu(II), however, insertion of Cu(II) into $Cu(II)LH_3^{2+}$ appears to be competitive with the initial exchange of Cu(II) for Na^+. As a result, to prepare $Cu(II)LH_3^{2+}$ uncontaminated by binuclear species, it is necessary to use a two-fold excess of $NaLH_3NO_3$ relative to the Cu(II) salt. By this modification, a Cu(II) mononuclear complex has been prepared and isolated as $Cu(II)LH_3(BF_4)_2 \cdot \frac{3}{2}H_2O$.

Mononuclear complexes of trivalent metals also have been prepared both directly by exchange of the trivalent metal cations as well as indirectly by exchange of a divalent metal cation followed by electrochemical oxidation to the trivalent state. Treatment of $NaLH_3NO_3$ with hydrated ferric chloride afforded $Fe(III)LH_3^{3+}$ which was isolated as a BF_4^- salt. The analogous Mn(III) complex was prepared by controlled potential electrolytic oxidation of $Mn(II)LH_3^{2+}$ prepared from $NaLH_3NO_3$ and Mn(II). In this case, $Mn(III)LH_3^{3+}$ was isolated as a ClO_4^- salt.

The last step in the multistep synthesis of binuclear clathrochelate complexes, $M(II)M(II)L^+$, is the insertion of a second metal ion into the mononuclear complexes, $M(II)LH_3(BF_4)_2 \cdot xH_2O$. In general, we found that addition of $M_B(II)$ salts to a solution of $M(II)LH_3(BF_4)_2 \cdot xH_2O$, in the presence of triethylamine, yielded the expected binuclear complexes, $M_A(II)M_B(II)LBF_4 \cdot xH_2O$ (eq 6). Using this approach, homo-

$$M_A(II) + M_B(II)LH_3(BF_4)_2 \cdot xH_2O \xrightarrow{\text{base}} M_A(II)M_B(II)LBF_4 \cdot xH_2O \quad (6)$$

binuclear complexes ($M_A = M_B$) of Mn(II), Fe(II), Co(II), Zn(II), and Cd(II) have been prepared. It is also possible to prepare these homo-

binuclear complexes more directly by reacting 2 equiv of a M(II) salt with 1 equiv of $NaLH_3NO_3$ under basic conditions. With the exception of Fe(II)Fe(II)L^+, however, this approach is unfruitful since a large fraction of the binuclear product precipitates as an insoluble NO_3^- salt. For Fe(II)Fe(II)L^+ prepared directly from $NaLH_3NO_3$, only a minimal amount of Fe(II)Fe(II)LNO_3 precipitates, which after removal leaves the bulk of the product for isolation as a BF_4^- salt.

Several attempts to prepare similar homobinuclear complexes of Ni(II), Mg(II), and Cu(II) by the insertion methods described above were unsuccessful. From reactions of either Ni(II)LH_3^{2+} or Mg(II)LH_3^{2+} with an excess of the appropriate M(II) salt, in the presence of various bases, only unreacted mononuclear complexes have been isolated. Such lack of reactivity is not a limitation in the case of Cu(II). In describing the preparation of Cu(II)LH_3^{2+}, it was noted that Cu(II) inserts facilely into Cu(II)LH_3^{2+} even in the absence of added base. The difficulty in preparing Cu(II)Cu(II)L^+ by the insertion methods described above is that one phenolic oxygen remains protonated and the binuclear complex Cu(II)Cu(II)$LH(BF_4)_2 \cdot 2H_2O$ is isolated. We found, however, that Cu(II)Cu(II)L^+ is isolable as a monohydrated BF_4^- salt if, instead of triethylamine, diisopropylethylamine is used as a co-solvent. Optimal yields have been obtained by first isolating Cu(II)Cu(II)$LH(BF_4)_2 \cdot 2H_2O$ under nearly neutral conditions and subsequently deprotonating the complex.

The primary utility of the insertion reaction (eq 6) is the preparation of heterobinuclear complexes ($M_A \neq M_B$). Using this reaction the following heteronuclear complexes have been prepared:

$Mn(II)M(II)L^{+}$, M = Co, Ni, Zn, Cd, and Mg; $Fe(II)M(II)L^{+}$, M = Mn, Co, Ni, Cu, Zn, Cd, and Mg; and $Cu(II)M(II)L^{+}$, M = Mn, Co, Ni, Cd, and Mg. For $Cu(II)ZnL^{+}$, it is necessary to use deprotonating conditions similar to those utilized in preparing $Cu(II)Cu(II)L^{+}$. In general, a minimal amount of scrambling (i.e., $2[M_A(II)LH_3^{2+}] + 2M_B(II) \rightarrow M_A(II)M_A(II)L^{+} + M_B(II)M_B(II)L^{+}$) was observed (vide infra) in the preparation of all these heteronuclear complexes. In many cases, however, there is a preferred method (i.e., $M_A(II) + M_B(II)LH_3^{2+}$ vs. $M_B(II) + M_A(II)LH_3^{2+}$) for preparing heteronuclear complexes which contain lesser quantities of homonuclear impurities. Details of the preferred methods are given in the Experimental Section.

In general, both homobinuclear and heterobinuclear complexes can be obtained as microcrystalline materials. However, only in the case of $Fe(II)Mn(II)LBF_4$ and $Fe(II)Co(II)LBF_4$ have crystals been obtained of sufficient quality for X-ray structural determination. Structural studies are presently being undertaken in collaboration with D. N. Hendrickson and co-workers.

Characterization

Infrared Spectroscopy. The infrared spectra of all binuclear complexes, M(II)M(II)L^+, are nearly indistinguishable and show features characteristic of metal-imine complexes.[16] Complete imine formation is indicated by the absence of aldehydic carbonyl-stretching bands in the 1660-1680 cm^{-1} region. The characteristic imine-stretching vibrations typically appear as three bands in the 1590-1640 cm^{-1} region. Typical separations and relative intensities of these bands are shown in Figure 2(a); Table I contains $\nu_{C=N}$ data for the homobinuclear compounds. In addition to imine-stretching bands, numerous unassigned ligand vibrations are observed in the 700-1640 cm^{-1} region.

For all other binuclear and mononuclear complexes of this type, infrared spectra are obtained which show features similar to those exhibited by M(II)M(II)L^+ complexes. For example, the infrared spectra of the M(II)LH_3^{2+} complexes show no significant changes as a function of the metal, but generally exhibit bands which are less well resolved than the corresponding M(II)M(II)L^+ complexes. An example of typical resolution is shown for imine-stretching bands in Figure 2(b).

Magnetic Susceptibility. Magnetic moments, μ_{eff}(295 K), of M(II)LH_3^{2+} and homonuclear M(II)M(II)L^+ complexes show that each metal ion is high spin in the solid state (Table I). Additionally, for Fe(III)$LH_3(BF_4)_3$ and selected heteronuclear complexes, magnetic moments also are consistent with high spin electronic configurations. In comparing μ_{eff}/M(II) values of homonuclear M(II)M(II)L^+ complexes with those of the corresponding M(II)LH_3^{2+} complexes, the binuclear μ_{eff}/M(II) values are slightly lower in all cases. This observation is

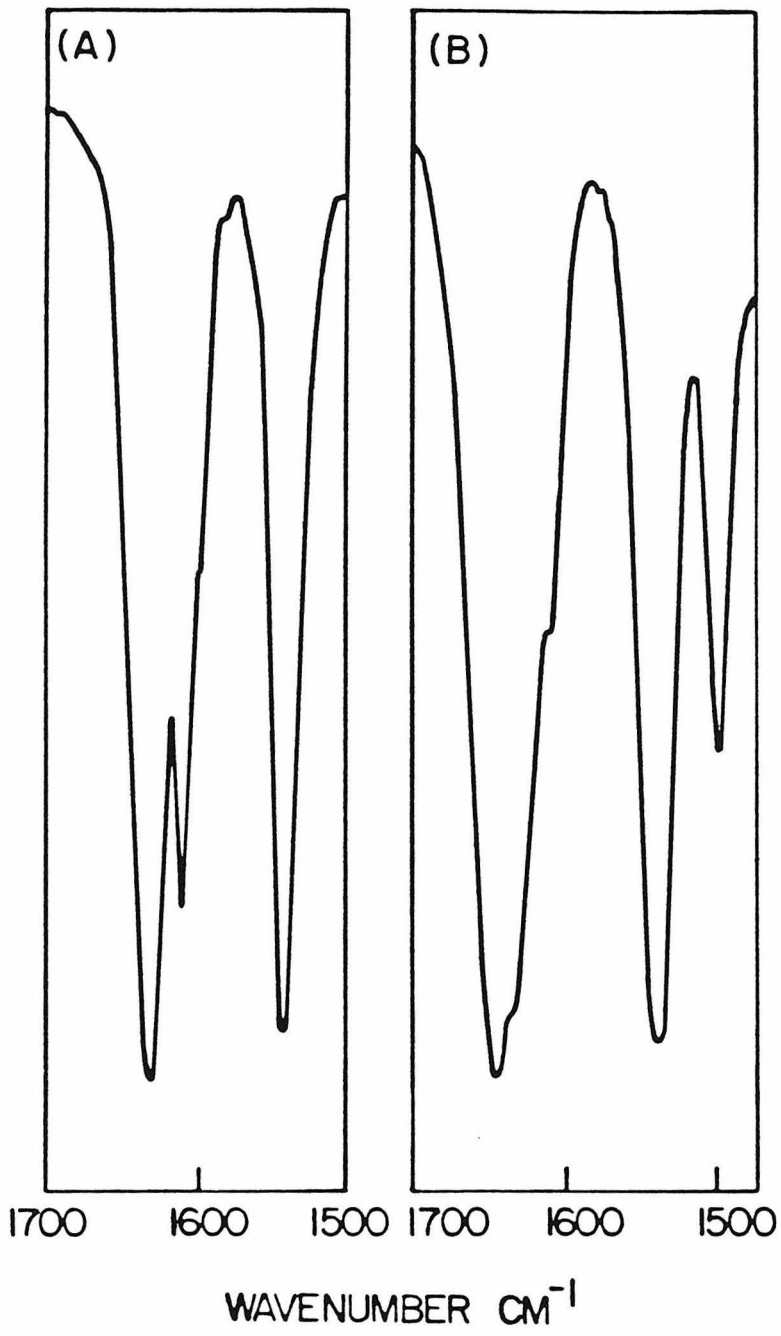


Figure 2. Infrared spectra showing $\nu_{C=N}$ stretching bands for (a) Mn(II)Mn(II)LBF_4 and (b) Mn(II)L$H_3(BF_4)_2 \cdot H_2O$.

Table I. Selected Infrared, Magnetic, and Conductivity Data for Binuclear and Mononuclear Complexes of L^{3-}, LH^{2-}, and LH_3.

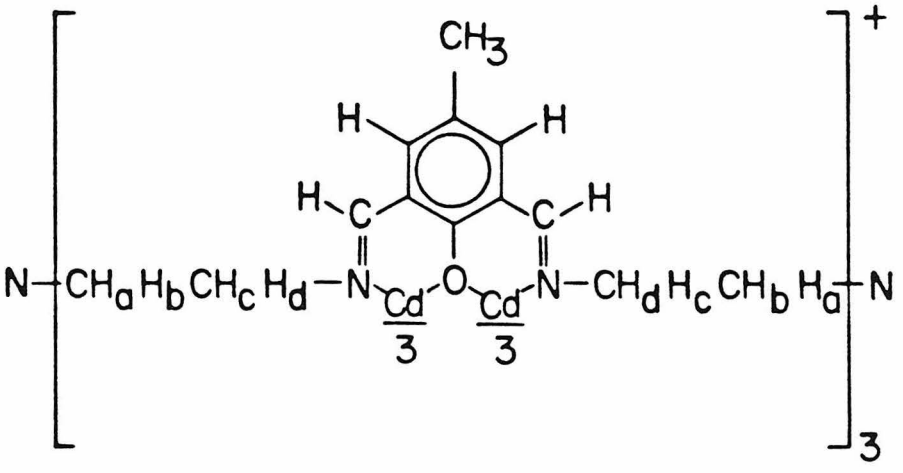
Complex	$\nu_{C=N}$, cm^{-1}	μ_{eff}/M (μ_B)	χ_M $cm^2 \cdot ohm^{-1} \cdot mol^{-1}$
$Mn(II)Mn(II)L^+$	1639, 1615, 1602 (sh)	5.59	72
$Fe(II)Fe(II)L^+$	1628, 1609, 1594 (sh)	5.18	66
$Co(II)Co(II)L^+$	1631, 1608, 1596	4.58	64
$Cu(II)Cu(II)L^+$	1643 (sh), 1630, 1611 (sh), 1600 (sh)	1.77	74
$Zn(II)Zn(II)L^+$		-	71
$Cd(II)Cd(II)L^+$		-	72
$Cu(II)Cu(II)LH^{2+}$		1.83	153
$Mn(II)LH_3^{2+}$		5.99	303
$Fe(II)LH_3^{2+}$		5.28	276
$Co(II)LH_3^{2+}$		5.06	307
$Ni(II)LH_3^{2+}$		3.19	276
$Cu(II)LH_3^{2+}$		1.80	316
$Zn(II)LH_3^{2+}$		-	306
$Cd(II)LH_3^{2+}$		-	275
$Mg(II)LH_3^{2+}$		-	301
$Fe(III)LH_3^{3+}$		5.88	389

consistent with some degree of antiferromagnetic metal-metal interaction in the binuclear species. Variable temperature susceptibility measurements confirm the antiferromagnetic nature of these interactions.[17]

NMR Spectroscopy. Of the homobinuclear complexes, M(II)M(II)L^{+}, only the diamagnetic Cd(II) complex is sufficiently soluble in several solvents to obtain suitable NMR spectra. Both ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra are consistent with a symmetrical clathrochelating solution structure (Table II). Two features of the ^{1}H NMR spectrum are particularly noteworthy. First, although the ethylene proton resonances are overlapping at 90-MHz, four inequivalent protons are resolved at 500-MHz (Figure 3). This observation of four signals is indicative of a static structure with rigid ethylene linkages. Geminal and vicinal coupling constants (Table II) were obtained by selective decoupling experiments and are comparable to values observed for similar rigid systems.[18] Also noteworthy is the splitting of one-fourth of the imine resonance into a satellite doublet. This observation is consistent with unresolved $^{111,113}Cd$-H coupling (for ^{111}Cd and ^{113}Cd, $I = \frac{1}{2}$, and relative abundances are 12.75% and 12.26%, respectively). Based on limited reports of $^{111,113}Cd$-H coupling[19] and similar behavior observed for Cd(II)LH_3^{2+}, the measured J value of 36 Hz is ascribed to three-bond coupling.

While the solubility of MLH_3^{n+} complexes is not a limitation in obtaining their ^{1}H NMR spectra, the spectra of the paramagnetic complexes are either extremely broad or complex; thus, tentative peak assignments have not been made. In contrast, spectra of diamagnetic

Table II. NMR[a] Data for Cd_2LBF_4.



Type	Assignment	Chemical shift, δ	Coupling
^1H[b,c]	CH_3	2.20 s	
	aryl	7.10 s	
	imine	8.23 s[d]	$J_{111,113CdH} = 36$
	H_a	2.61 m	$J_{H_aH_b} = 13.4$
			$J_{H_aH_c} = 2.7$
	H_b	2.85 m	$J_{H_aH_d} = 12.3$
			$J_{H_bH_c} = 1.1$
	H_c	3.02 m	$J_{H_bH_d} = 2.4$
			$J_{H_cH_d} = 11.0$
	H_d	3.59 m	$J_{H_dH_{imine}} = 1.0$
$^{13}C\{^1H\}$[e]	CH_3	19.2	
	CH_aH_b, CH_cH_d	57.6, 59.0	
	aryl	119.9, 121.8,	
		140.9, 169.3	
	imine	171.1	

Table II. (continued)

[a]NMR spectra were obtained at ambient temperature. Chemical shifts are reported in ppm relative to internal Me_4Si; coupling constants are reported in hertz.

[b]Spectrum was taken in acetonitrile-$\underline{d}_3$.

[c]The alkyl region of this spectrum is interpretable only at 500 MHz; see Figure 2. Tentative assignments were made by selective decoupling experiments (coupling constants ± 1 Hz).

[d]A satellite doublet due to ^{111,113}Cd-H coupling also was observed.

[e]Spectrum taken in dimethylsulfoxide-$\underline{d}_6$.

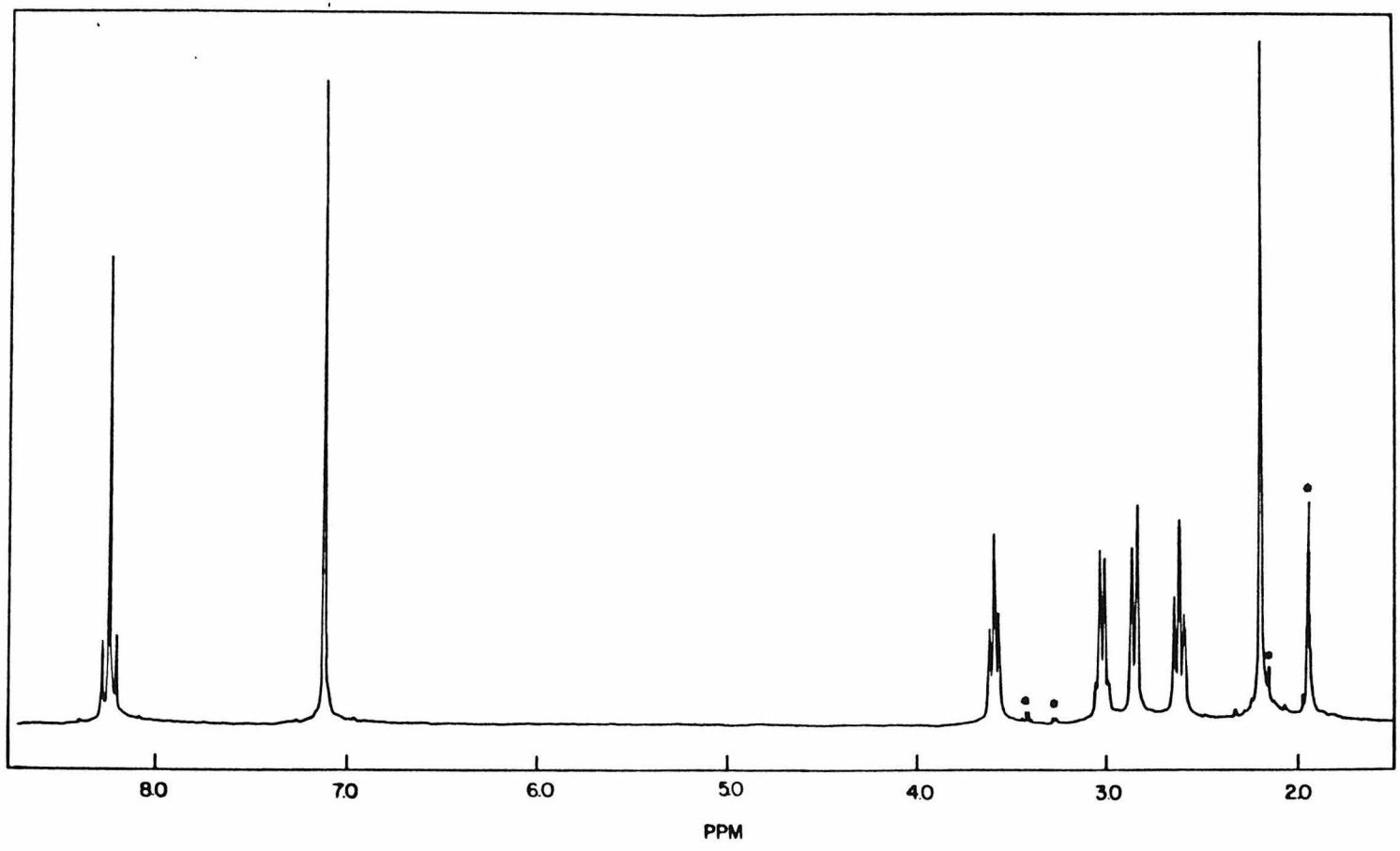
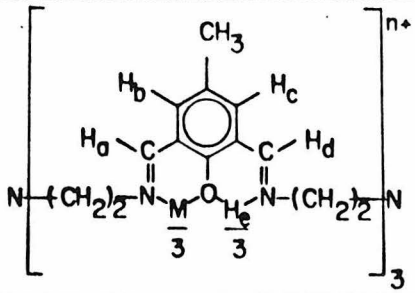


Figure 3. 500 MHz ^{1}H NMR spectrum of Cd(II)Cd(II)LBF$_4$. The four inequivalent -CH_2CH_2- protons are resolved and appear at 2.6, 2.8, 3.0, and 3.6 ppm (δ). Asterisks denote solvent impurities.

MLH_3^{n+} complexes are interpretable and provide structural information on these complexes. The ^1H NMR for all diamagnetic MLH_3^{2+} complexes show similar features and are consistent with a symmetrical clathrochelating structure, containing a metal ion in one site and three phenolic protons in the other site (Table III). The phenolic protons (H_e) typically appear as a single broad (>100 Hz fwhm) downfield resonance which is resolvable as a doublet only at high R_f power. By deuterium exchange, it was established that the splitting of the H_e resonance is due to coupling to an imine proton (Hd, Table III). These observations are consistent with intracavity hydrogen bonding of the phenolic protons to proximal imine nitrogens, with the broadness of the H_e resonance being attributed to ^{14}N quadrupolar broadening. For $Cd(II)LH_3^{2+}$, additional coupling of ^{111}Cd and ^{113}Cd nuclei to the other set of three imine protons (H_a) is observed. The J value of 37 Hz for this unresolved $^{111,113}Cd$-H coupling is similar to that observed for $Cd(II)Cd(II)L^+$ (36 Hz).

The ^1H NMR of $NaLH_3NO_3$ have been examined in several different solvents. In methylene chloride-$\underline{d}_2$, the spectrum of $NaLH_3NO_3$ is similar to those of diamagnetic $M(II)LH_3^{2+}$ complexes in acetonitrile-$\underline{d}_3$, exhibiting inequivalent aryl (H_b and H_c) and imine (H_a and H_d) resonances (Table III). As these spectra have been interpreted, the metal ions are chelated in one of two available sites and are not undergoing either site-site exchange or dissociative metal ligand processes on the NMR time scale. In contrast, the spectrum of $NaLH_3NO_3$ in methanol-$\underline{d}_4$ or acetonitrile-$\underline{d}_3$ shows two broad resonances at ~7.1 and ~8.5 ppm corresponding to the aryl and imine protons, respectively. This

Table III. ^{1}H NMR[a] Data for MLH_3^{n+} Complexes



Assignment	$NaLH_3NO_3$[b]		Complex: $Cd(II)LH_3(BF_4)_2 \cdot H_2O$[c]		$Zn(II)LH_3(BF_4)_2 \cdot H_2O$[c]		$Mg(II)LH_3(BF_4)_2 \cdot H_2O$[c]	
H_a, s	8.21		8.33[d]	$J_{111,113CdH} = 37$	8.29		8.23	
H_b, d	7.09	$J_{H_bH_c} = 2$	7.33	$J_{H_bH_c} = 2$	7.34	$J_{H_bH_c} = 2$	7.55	$J_{H_bH_c} = 2$
H_c, d	7.22		7.50		7.51		7.35	
H_d, d	8.25	$J_{H_dH_e} = 7$	8.34	$J_{H_dH_e} = 14$	8.36	$J_{H_dH_e} = 14$	8.40	$J_{H_dH_e} = 14$
H_e, br	13.5		13.9		13.9		13.6	
CH_3, s	2.25		2.12		2.19		2.36	
$(CH_2)_2$[e]	1.8-4.1		1.8-4.1		1.7-4.0		1.9-4.1	

Table III (continued)

[a] ^{1}H NMR spectra were taken at ambient temperature except where indicated. Chemical shifts (δ) are reported in ppm relative to internal Me_4Si; coupling constants are reported in hertz.

[b] Spectrum was taken at 10° C in methylene chloride-$\underline{d}_2$.

[c] Spectra were taken in acetonitrile-$\underline{d}_3$.

[d] A satellite doublet due to ^{111,113}Cd-H coupling also was observed.

[e] A range of chemical shifts is given since the 8 inequivalent alkyl protons are unresolved at 90 MHz.

observation strongly suggests that under these conditions the complex is undergoing rapid, reversible metal-ligand dissociation and/or the Na^+ ion is exchanging between the two sites without dissociating from the ligand. This type of NMR behavior is similar to that observed by J. M. Lehn and co-workers for 2:1 cryptate/alkali-cation-salt mixtures in aqueous solutions.[20]

Conductivity. Molar conductivities, Λ_M, for mononuclear and binuclear complexes of this type are generally within the expected ranges (Table I).[21] For example, the homonuclear complexes, $M(II)M(II)LBF_4 \cdot xH_2O$, in DMF solutions have Λ_M values (64-74 $cm^2 \cdot mol^{-1} \cdot ohm^{-1}$) consistent with those of 1:1 salts (60-80 $cm^2 \cdot mol^{-1} \cdot ohm^{-1}$). Also determined in DMF, the anomalous homobinuclear species, $Cu(II)Cu(II)LH(BF_4)_2 \cdot 2H_2O$, gives a Λ_M value (153 $cm^2 \cdot mol^{-1} \cdot ohm^{-1}$) within the normal range for 2:1 electrolytes (130-170 $cm^2 \cdot mol^{-1} \cdot ohm^{-1}$). For mononuclear complexes, $M(II)LH_3(BF_4)_2 \cdot xH_2O$, in acetonitrile solutions, molar conductivities vary from 275 to 316 $cm^2 \cdot mol^{-1} \cdot ohm^{-1}$. This range is slightly higher than that expected for 2:1 electrolytes in acetonitrile (220-300 $cm^2 \cdot mol^{-1} \cdot ohm^{-1}$), although values as high as 336 $cm^2 \cdot mol^{-1} \cdot ohm^{-1}$ have been observed previously in several cases.[21] For $Fe(III)LH_3(BF_4)_3$ in acetonitrile, the Λ_M value (389 $cm^2 \cdot mol^{-1} \cdot ohm^{-1}$) falls within the expected range for 3:1 electrolytes (340-420 $cm^2 \cdot mol^{-1} \cdot ohm^{-1}$).

Elemental Analysis. All of the complexes reported here have been analyzed for C, H, and N, and gave satisfactory analyses (Table IV). Additionally, most complexes have been analyzed for the

Table IV. Analytical Data for $M_A(II)M_A(II)L^+$, $M_A(II)M_B(II)L^+$, and $M_ALH_3^{n+}$ Complexes.

Complex	Found (Calcd.) (%)				
	C	H	N	M_A	M_B
$Mn(II)Mn(II)LBF_4$	53.96(53.80)	5.24(5.21)	12.74(12.87)	12.99(12.62)	
$Fe(II)Fe(II)LBF_4$	53.82(53.70)	5.29(5.20)	13.17(12.84)	13.10(12.80)	
$Co(II)Co(II)LBF_4 \cdot H_2O$	52.24(52.24)	5.11(5.28)	12.59(12.49)	13.08(13.14)	
$Cu(II)Cu(II)LBF_4 \cdot H_2O$	51.78(51.71)	5.49(5.23)	12.05(12.37)	13.84(14.03)	
$Zn(II)Zn(II)LBF_4$	52.46(52.55)	5.14(5.09)	12.70(12.57)	13.87(14.67)	
$Cd(II)Cd(II)LBF_4$	47.44(47.53)	4.69(4.60)	11.44(11.37)	22.88(22.81)	
$Cu(II)Cu(II)LH(BF_4)_2 \cdot 2H_2O$	46.64(46.31)	5.02(4.98)	11.17(11.08)	12.54(12.56)	
$Mn(II)LH_3(BF_4)_2 \cdot H_2O$	50.70(50.73	5.26(5.45)	12.35(12.13)	5.88(5.94)	
$Fe(II)LH_3(BF_4)_2 \cdot H_2O$	50.66(50.67)	5.21(5.45)	12.27(12.12)	6.22(6.04)	
$Co(II)LH_3(BF_4)_2 \cdot H_2O$	50.47(50.50)	5.40(5.43)	12.38(12.08)	6.10(6.35)	
$Ni(II)LH_3(BF_4)_2 \cdot H_2O$	50.32(50.52)	5.16(5.44)	12.07(12.08)	6.13(6.33)	
$Cu(II)LH_3(BF_4)_2 \cdot \frac{3}{2}H_2O$	49.87(49.77)	5.36(5.46)	11.97(11.90)	6.49(6.75)	
$Zn(II)LH_3(BF_4)_2 \cdot H_2O$	50.10(50.16)	5.26(5.07)	12.05(11.99)	6.76(7.00)	
$Cd(II)LH_3(BF_4)_2 \cdot H_2O$	47.93(47.75)	5.24(5.14)	11.35(11.42)	11.06(11.42)	

Table IV. (continued)

Complex	Found (Calcd.) (%) C	H	N	M_A	M_B
$Mg(II)LH_3(BF_4)_2 \cdot H_2O$	52.81(52.46)	5.56(5.64)	12.45(12.55)	2.58(2.72)	
$Mn(III)LH_3(ClO_4)_3$	45.80(45.47)	4.87(4.70)	10.99(10.88)		
$Fe(III)LH_3(BF_4)_3$	47.34(47.31)	5.02(4.89)	11.11(11.31)	5.52(5.64)	
$Fe(II)Mn(II)LBF_4$	53.73(53.75)	5.28(5.20)	12.90(12.85)	6.16(6.40)	6.34(6.30)
$Fe(II)Co(II)LBF_4$	53.56(53.50)	5.16(5.18)	13.02(12.80)	6.38(6.37)	
$Fe(II)Ni(II)LBF_4$	53.36(53.52)	5.18(5.18)	13.11(12.80)		6.55(6.70)
$Fe(II)Cu(II)LBF_4$	53.42(53.23)	5.16(5.15)	13.04(12.73)	6.28(6.34)	6.84(7.22)
$Fe(II)Zn(II)LBF_4 \cdot H_2O$	52.01(52.05)	5.26(5.26)	12.56(12.45)	5.87(6.20)	7.11(7.26)
$Fe(II)Cd(II)LBF_4$	50.82(50.43)	5.03(4.88)	12.26(12.06)	5.98(6.01)	12.05(12.10)
$Fe(II)Mg(II)LBF_4$	55.48(55.71)	5.56(5.39)	13.53(13.32	6.02(6.64)	2.59(2.89)
$Cu(II)Mn(II)LBF_4 \cdot H_2O$	51.95(52.21)	5.20(5.28)	12.51(12.49)	6.82(7.08)	5.78(6.12)
$Cu(II)Co(II)LBF_4 \cdot \frac{1}{2}H_2O$	52.21(52.51)	5.21(5.19)	12.56(12.56)		
$Cu(II)Ni(II)LBF_4 \cdot \frac{1}{2}H_2O$	52.41(52.52)	5.23(5.19)	12.58(12.56)	6.83(7.12)	6.41(6.58)
$Cu(II)Zn(II)LBF_4 \cdot H_2O$	51.57(51.61)	5.23(5.22)	12.35(12.34)	6.30(7.00)	7.50(7.20)
$Cu(II)Cd(II)LBF_4$	49.75(50.01)	4.89(4.84)	12.01(11.96)	6.46(6.78)	11.88(12.00)

Table IV. (continued)

Complex	Found (Calcd.) (%) C	H	N	M_A	M_B
$Cu(II)Mg(II)LBF_4 \cdot \frac{3}{2}H_2O$	53.45(53.50)	5.34(5.53)	12.88(12.80)	7.07(7.26)	2.58(2.78)
$Mn(II)Ni(II)LBF_4$	53.26(53.57)	5.35(5.19)	13.06(12.81)		6.68(6.72)
$Mn(II)Zn(II)LBF_4$	53.28(53.17)	5.19(5.14)	12.87(12.71)	6.16(6.23)	7.35(7.42)
$Mn(II)Cd(II)LBF_4$	50.83(50.47)	4.96(4.88)	12.32(12.08)		12.29(12.11)
$Mn(II)Mg(II)LBF_4$	55.63(55.77)	5.44(5.40)	13.38(13.34)		2.87(2.89)

appropriate metals. For the heteronuclear complexes, metal analyses generally are consistent with the expected formulations. It should be noted, however, that these data cannot be used to distinguish between pure heteronuclear complexes, $M_A(II)M_B(II)L^+$, and samples which contain significant equimolar amounts of homonuclear complexes, $M_A(II)M_A(II)L^+$ and $M_B(II)M_B(II)L^+$. For the purpose of determining the heteronuclear purity of these samples, the electrochemical methods described below have been used.

Mössbauer Spectroscopy. The 4.2 K ^{57}Fe Mössbauer spectrum of $Fe(II)Fe(II)L^+$ shows only one quadrupole-split doublet for which a least squares fit yields a quadrupole splitting of ΔE_Q = 0.9601(19) mm/sec and an isomer shift of δ = 0.4870(9) mm/sec vs. iron metal. Contamination of the sample by Fe(III) ions is not observed. The ΔE_Q value is lower than those values typically observed for six-coordinate, high-spin Fe(II) complexes (2.0-3.0 mm/sec).[22] Abnormally low ΔE_Q values generally are indicative of either metal-ligand covalent bonding or highly symmetric ligand environments.[23] For Fe(II) ions in L^{3-}, the latter explanation appears to be more plausible.

Electrochemistry. Cyclic voltammetry and differential pulse voltammetry were used to characterize the electrochemical behavior at a platinum electrode of both mononuclear and binuclear complexes. Formal potentials (E^f) were measured and are reported with respect to an internal reference standard,[24] the ferricenium/ferrocene couple (Fc^+/Fc). For complexes with limited solubility, potentials could be measured with greater precision using differential pulse voltammetry instead of cyclic voltammetry. For this reason, formal potentials

cited in the text are the differential pulse voltammetric values (E^P). It should be noted, however, that potentials obtained by one technique differ by 15 mV or less with respect to the other technique.

The electrochemical results for all of the binuclear complexes reported here were obtained in DMF solutions. For the series of homonuclear complexes, M(II)M(II)L^+ (M = Mn, Fe, Co, Cu, Zn, and Cd), only the Mn(II), Fe(II), and Cu(II) complexes yielded cyclic voltammograms with quasi-reversible metal waves. Several overlapping, irreversible waves were observed for Co(II)Co(II)L^+, and only ligand reduction waves at very negative potentials (<-2.0 V) appeared in cyclic voltammograms of Zn(II)Zn(II)L^+ and Cd(II)Cd(II)L^+. Of the three complexes exhibiting quasi-reversible metal waves, only for Fe(II)Fe(II)L^+ were two waves observable corresponding to sequential one-electron processes at the two interacting metal centers (Figure 4). These waves, ascribed to successive oxidations of Fe(II)Fe(II)L^+ to Fe(II)Fe(III)L^{2+} and then to Fe(III)Fe(III)L^{3+}, have measured formal potentials of -0.553 V and +0.133 V vs. Fc^+/Fc, respectively. For anodic scans of Mn(II)Mn(II)L^+, the oxidation wave of one Mn(II) at +0.120 V is followed by an irreversible wave at a potential ~ 0.5 V more positive. Since this second wave occurs at similar potentials in scans of Mn(II)M(II)L^+ (M = Ni, Zn, Cd, and Mg), it is ascribed to an oxidative ligand process. For cathodic scans of Cu(II)Cu(II)L^+, a reduction wave at -1.083 V attributed to the Cu(II)Cu(II)L^+/Cu(I)Cu(II)L couple is succeeded at a potential ~ 0.85 V more negative by an irreversible wave. This second wave is absent in scans of heteronuclear Cu(II)M(II)L^+ complexes and probably

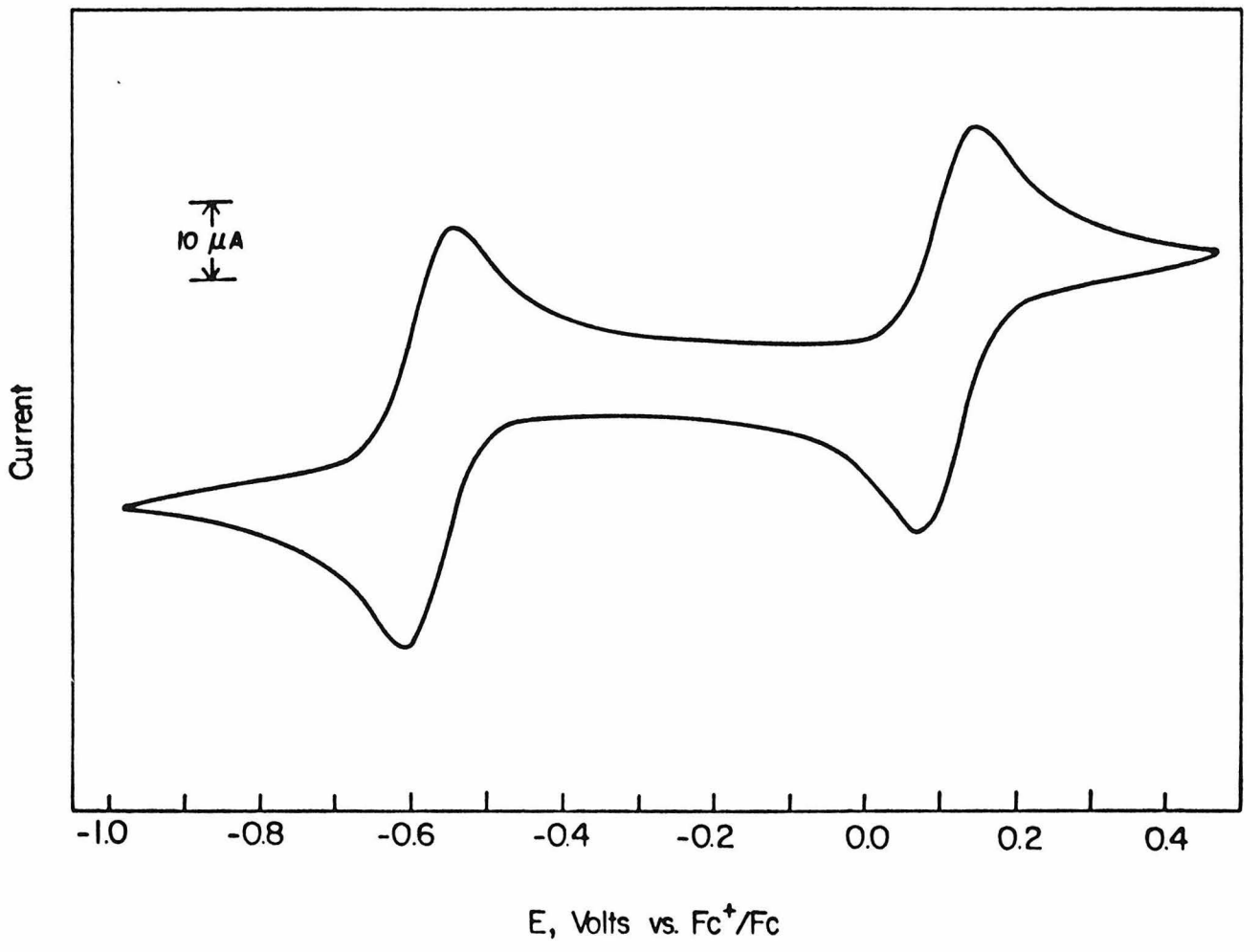


Figure 4. Cyclic voltammogram of $Fe(II)Fe(II)LBF_4$. The wave at ~ -0.6 V is the $Fe(III)Fe(II)L^{2+}$/ $Fe(II)Fe(II)L^{+}$ wave, while the $Fe(III)Fe(III)L^{3+}/Fe(III)Fe(II)L^{2+}$ couple appears at ~0.1 V.

corresponds to the reduction of Cu(I)Cu(II)L to Cu(I)Cu(I)L^-. That all the quasi-reversible metal waves were one-electron processes was verified by coulometry ($\underline{n}$ values = 1.0 ± 0.05).

Electrochemical methods were invaluable for establishing the purity of heteronuclear $M_A(II)M_B(II)L^+$ complexes, as has been reported previously.[1] In general, it is observed that the redox potentials for electroactive metals in heteronuclear complexes differ measurably from those in the potentially contaminating, corresponding homonuclear complexes. For example, for Fe(II)Cu(II)L^+, a single Fe(III)/Fe(II) wave at -0.505 V and a single Cu(II)/Cu(I) wave at -1.099 V are observed (Figure 5). A lack of contamination by Fe(II)Fe(II)L^+ is indicated by the absence of a shoulder at -0.553 V. Similarly, although less conclusively since the potentials differ only slightly, purity with respect to Cu(II)Cu(II)L^+ contamination is established by the absence of a shoulder at -1.083 V. In general, for heteronuclear complexes prepared by methods described in the Experimental Section, homonuclear contamination is estimated at less than 5% using this electrochemical testing method.

The reduction potentials of the Mn(III)/Mn(II), Fe(III)/Fe(II), and Cu(II)/Cu(I) as a function of remote metal, $M_B(II)$, in $M_A(II)M_B(II)L^+$ complexes are reported in Tables V, VI, and VII, respectively. A description of the characteristic electrochemical behavior for each series follows:

M(III)/Mn(II). As examined by cyclic voltammetry, the Mn(III/II) waves are quasi-reversible for a range of scan rates (20-500 mV/sec). A typical wave shape is shown for this couple in

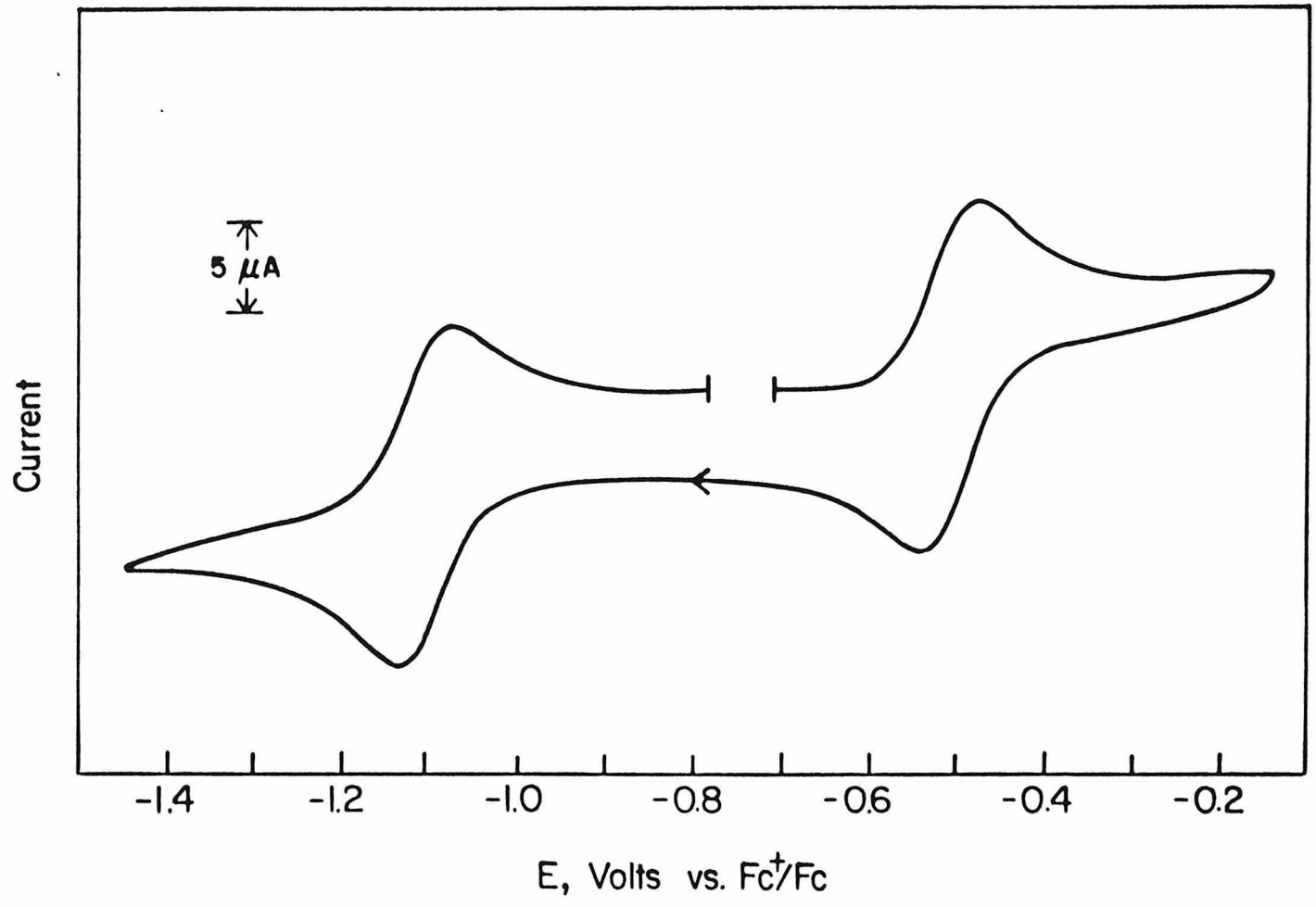


Figure 5. Cyclic voltammogram of Fe(II)Cu(II)LBF$_4$. The wave at ~ -1.1 V is the Cu(II)/Cu(I) wave, while the Fe(III)/Fe(II) couple appears at ~ -0.55 V.

Table V. Reduction Potentials for the Mn(III)/Mn(II) Couple as a Function of Remote Metal M_B(II) (measured in DMF vs. Fc^+/Fc).

Complex	Cyclic Voltammetry		Differential Pulse Voltammetry
	$E^f(V)^a$	$E_{p_a} - E_{p_c}(mV)^b$	$E^P(V)^c$
$Mn(II)Mn(II)L^+$	0.120	71	0.114
$Mn(II)Ni(II)L^+$	0.363	90[d]	0.370
$Mn(II)Cu(II)L^+$	-0.062	81	-0.053
$Mn(II)Zn(II)L^+$	0.018	87	0.028
$Mn(II)Cd(II)L^+$	0.036	70	0.048
$Mn(II)Mg(II)L^+$	0.281	86	0.285

[a]Formal potentials are reported using $E^f = (E_{p_a} - E_{p_c})/2$ and were measured at a scan rate of 200 mV/sec.

[b]Anodic peak to cathodic peak separations are reported for the minimum observed separations in the scan-rate range of 20-500 mV/sec.

[c]Peak potentials were measured at a scan rate of 1 mV/sec.

[d]This value can only be estimated because of the low solubility of the complex and the proximity of the metal wave to a ligand wave.

Table VI. Reduction Potentials for the Fe(III)/Fe(II) Couple as a Function of Remote Metal M_B(II) (measured in DMF vs. Fc^+/Fc).

Complex	Cyclic Voltammetry[a]		Differential Pulse Voltammetry
	E^f(V)	$E_{p_a} - E_{p_c}$(mV)	E^P(V)[b]
Fe(II)Mn(II)L^+	-0.506	68	-0.511
Fe(II)Fe(II)L^+	-0.557	68	-0.553
Fe(II)Co(II)L^+	-0.548	68	-0.557
Fe(II)Ni(II)L^+	-0.357	71	-0.365
Fe(II)Cu(II)L^+	-0.499	69	-0.505
Fe(II)Zn(II)L^+	-0.586	70	-0.590
Fe(II)Cd(II)L^+	-0.555	75	-0.564
Fe(II)Mg(II)L^+	-0.397	68	-0.401

[a]See footnotes (a) and (b) for Table V.

[b]Peak potentials were measured at 0.5 mV/sec.

Table VII. Reduction Potentials for the Cu(II)/Cu(I) Couple as a Function of Remote Metal M_B (measured in DMF vs. Fc^+/Fc).

Complex	Cyclic Voltammetry[a]		Differential Pulse Voltammetry
	E^f(V)	$E_{p_a} - E_{p_c}$(mV)	E^P(V)[b]
Cu(II)Mn(II)L^+	-1.070	83	-1.084
Cu(II)Fe(II)L^+	-1.089	73	-1.099
Cu(II)Co(II)L^+	-1.001	81	-1.015
Cu(II)Ni(II)L^+	-0.938	79	-0.942
Cu(II)Cu(II)L^+	-1.077	101	-1.083
Cu(II)Zn(II)L^+	-1.086	99	-1.092
Cu(II)Cd(II)L^+	-1.186	85	-1.188
Cu(II)Mg(II)L^+	-0.997	81	-1.001

[a] See footnotes (a) and (b) for Table V.

[b] Peak potentials were measured at 0.5 mV/sec.

Figure 6. Peak potential separations ($E_{p_a} - E_{p_c}$) show only a slight scan-rate dependence. For the series, the average minimum $E_{p_a} - E_{p_c}$ is 80 mV[25] in comparison with the Nernstian value of 59 mV.[26] Formal potentials vary over a range of ~425 mV. Mn(III)/Mn(II) potentials have not been observed and therefore are not reported for $Mn(II)Fe(II)L^+$ and $Mn(II)Co(II)L^+$. For these complexes only the more negative potential M(III)/M(II) waves of iron and cobalt (irreversible) have been observed.

Fe(III)/Fe(II). Scan-rate independent Fe(III)/Fe(II) waves with an average minimum $E_{p_a} - E_{p_c}$ of 71 mV have been observed by cyclic voltammetry. These Fe(III)/Fe(II) waves, exhibiting nearly reversible behavior, have potentials which vary over a range of ~225 mV. A typical cyclic voltammogram for this redox couple is shown in Figure 7.

Cu(II)/Cu(I). In comparison with Mn(III)/Mn(II) and Fe(III)/Fe(II) waves, Cu(II)/Cu(I) waves are the least reversible with a minimum $E_{p_a} - E_{p_c}$ of 85 mV. A typical wave shape for the Cu(II)/Cu(I) couple is shown in Figure 8. For $Cu(II)M(II)L^+$ complexes (M = Mn, Fe, and Co), waves are observable for both metal centers. Characteristics of the Mn(III)/Mn(II) and Fe(III)/Fe(II) waves are included in the previously described series; the Co(III)/Co(II) wave is quasi-reversible with E^f = -0.246 V and $E_{p_a} - E_{p_c}$ = 90 mV. The Cu(II)/Cu(I) potentials vary over a range of ~250 mV.

Cyclic voltammograms obtained for the series of mononuclear complexes $M(II)LH_3^{2+}$ (M = Mn, Fe, Co, Ni, Cu, Zn, Cd, and Mg), featured broad ligand waves for which both anodic and cathodic peak currents were not observed. In acetonitrile solutions, non-irreversible

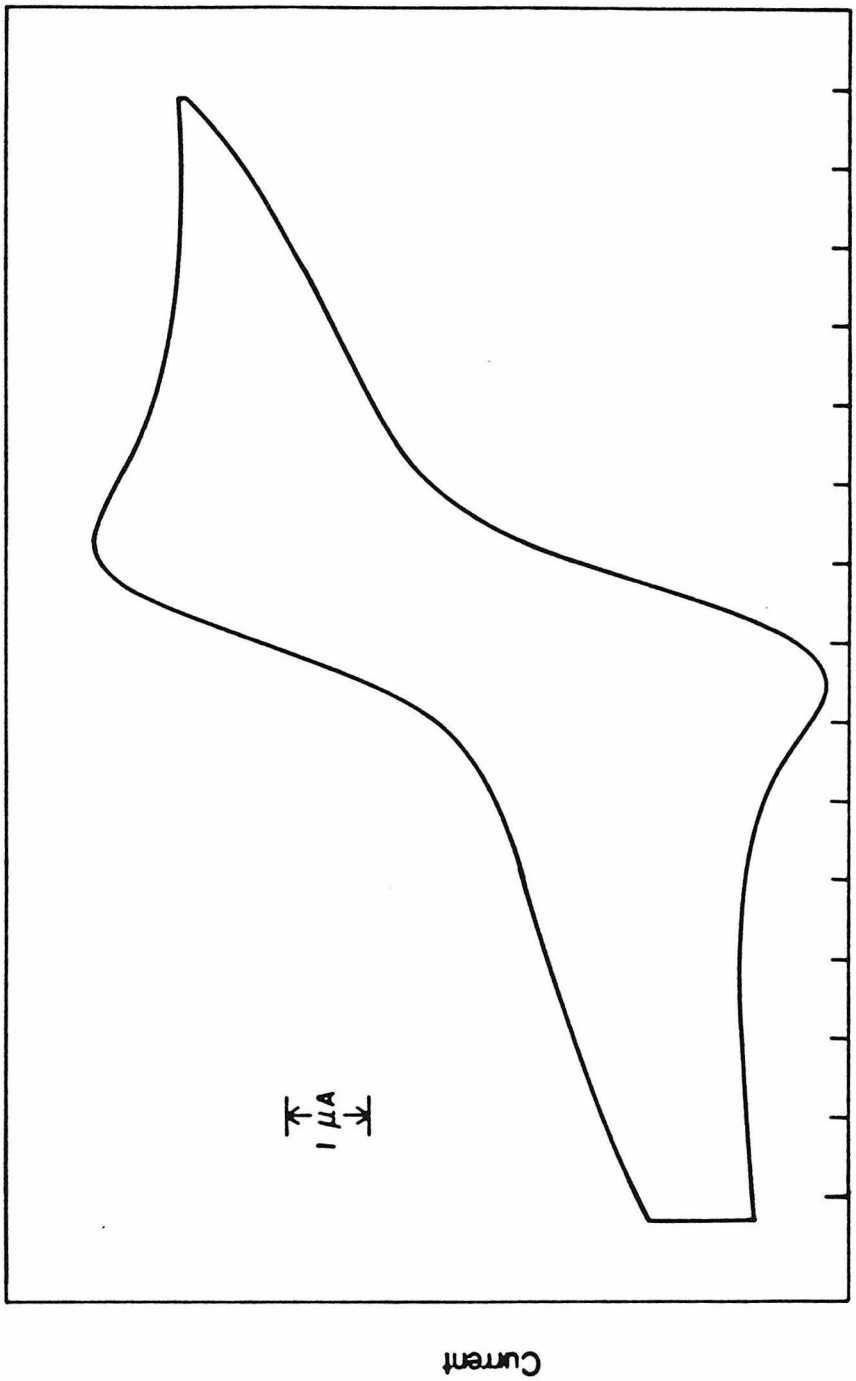


Figure 6. Typical cyclic voltammogram for Mn(III)/Mn(II) couple in $Mn(II)M(II)L^{+}$ complexes.

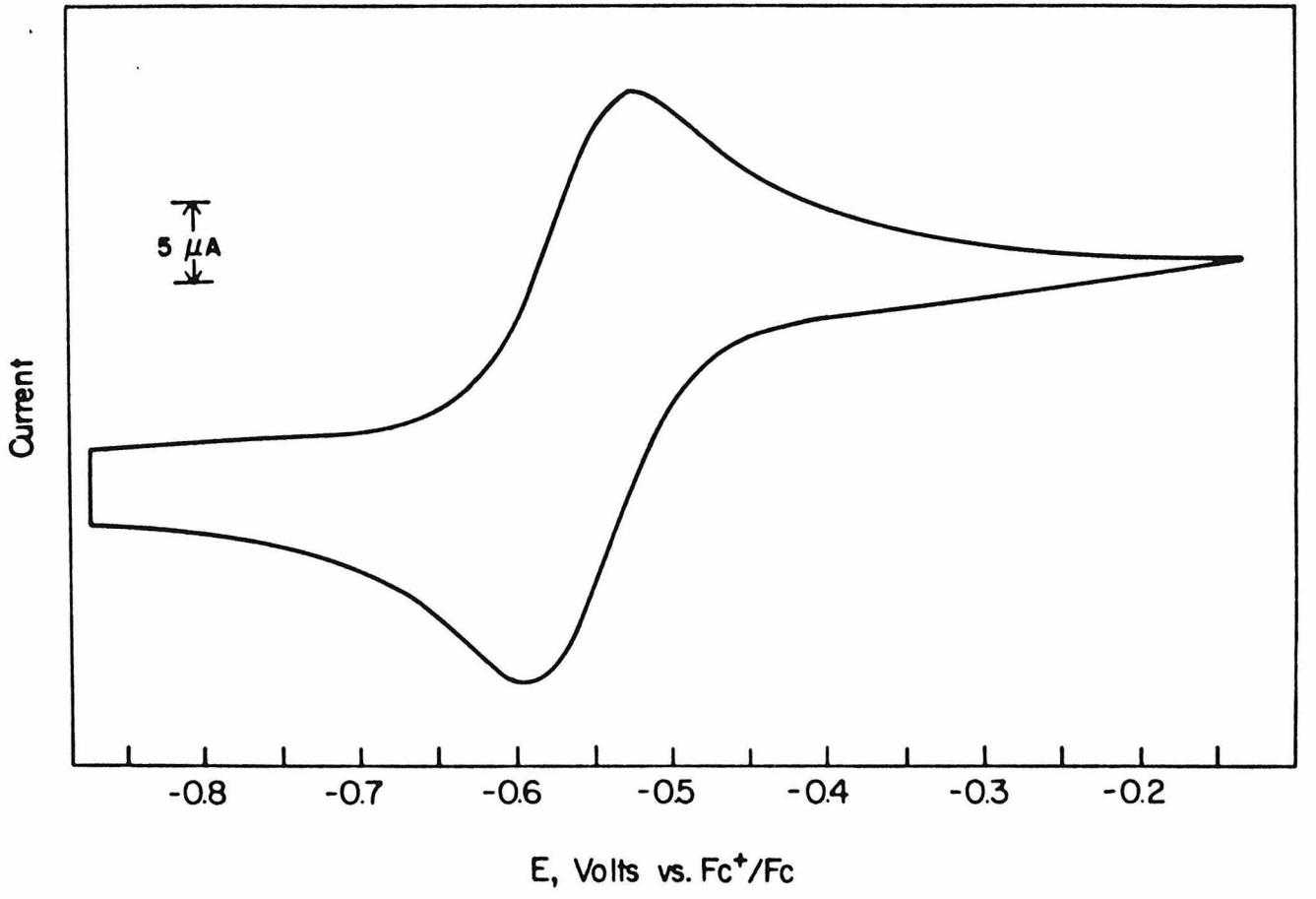


Figure 7. Typical cyclic voltammogram for Fe(III)/Fe(II) couple in $Fe(II)M(II)L^{+}$ complexes.

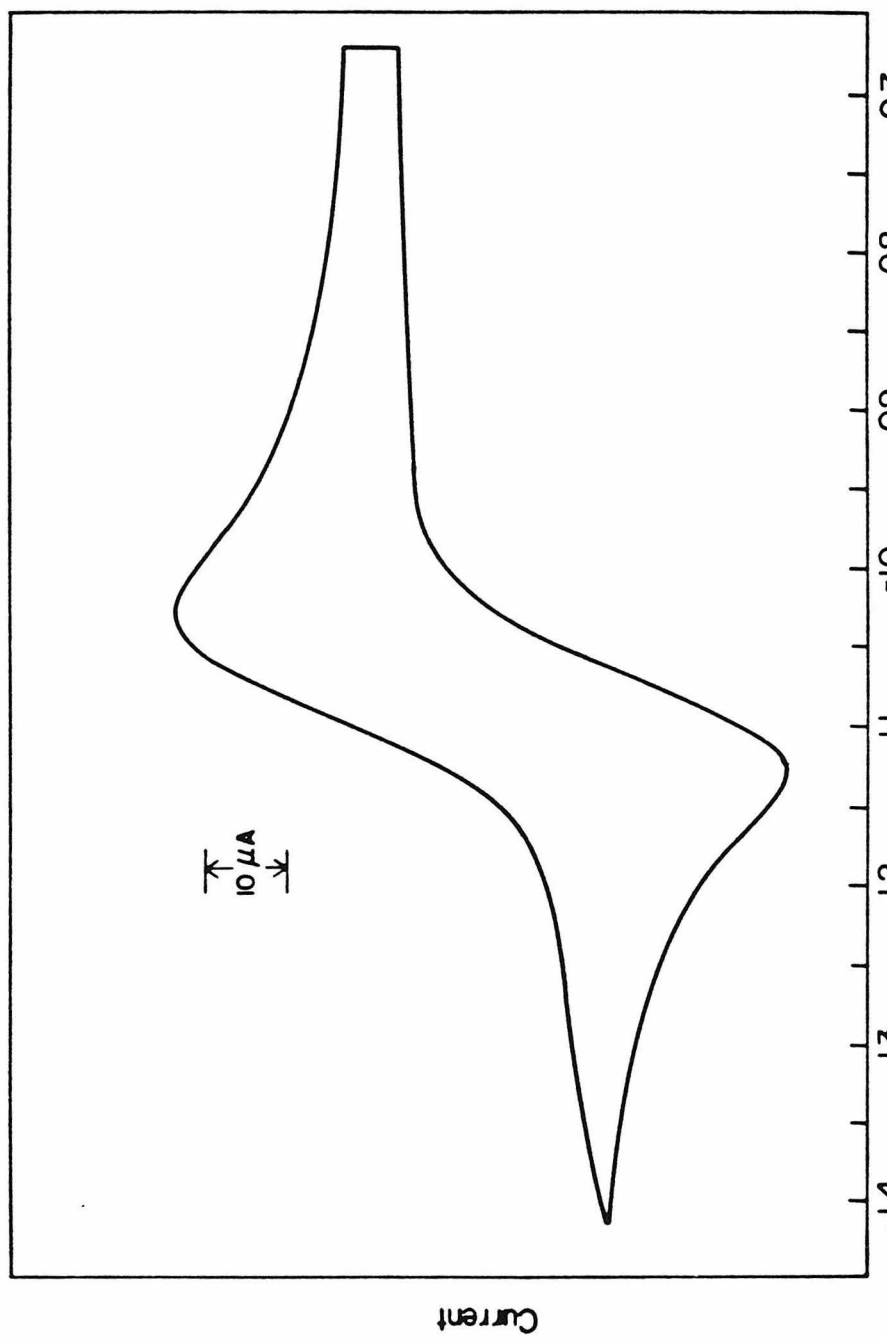


Figure 8. Typical cyclic voltammogram for Cu(II)/Cu(I) couple in $Cu(II)M(II)L^{+}$ complexes.

metal waves could be observed only for the Mn(II), Fe(II), and Co(II) complexes, corresponding to a M(III)/M(II) couple (Table VIII). Of these complexes, a quasi-reversible metal wave with a minimum $E_{p_a} - E_{p_c}$ less than 130 mV was observed only for $Fe(II)LH_3^{2+}$. Despite substantial broadness of the Mn(III)/Mn(II) and Co(III)/Co(II) waves, coulometric experiments indicated that the waves represent chemically reversible, one-electron processes ($\underline{n}$ values = 1.0 ± 0.05).

Table VIII. Electrochemical Data for the M(III)/M(II) Couple of $M(II)LH_3^{2+}$ Complexes[a]

Complex	Cyclic Voltammetry[b]		Differential Pulse Voltammetry	Coulometric[d]
	E^f(V)	$E_{p_a} - E_{p_c}$(mV)	E^P(V)[c]	n value
$Mn(II)LH_3^{2+}$	0.309	130	0.301	1.05
$Fe(II)LH_3^{2+}$[e]	-0.283	75	-0.287	0.96
$Co(II)LH_3^{2+}$	0.085[f]	>400	ND[g]	1.02

[a]All measurements were taken with acetonitrile as the solvent. Formal potentials are reported vs. Fc^+/Fc.

[b]See footnotes (a) and (b) for Table V.

[c]Peak potentials were measured at a scan rate of 1 mV/sec.

[d]These values were determined by controlled potential electrolysis at potentials 20-30 mV positive of E_{p_a}.

[e]The electrochemical results reported for $Fe(II)LH_3^{2+}$ are an average of the data obtained for both $Fe(II)LH_3^{2+}$ and $Fe(III)LH_3^{3+}$.

[f]This value only can be estimated since $(E_{p_a} - E_{p_c})$ is >400 mV.

[g]ND = not determined.

DISCUSSION

Clathrochelates and Template Reactions. Two general types of clathrochelates have been reported prior to the preparation and characterization of the mononuclear and binuclear clathrochelates described in this report. The first type is flexible mononuclear and binuclear complexes which can be prepared directly by adding metal ions to solutions containing clathrochelating polyether/polyamine ligands. These ligands, referred to as both cryptates and cryptands, have been prepared and their coordination chemistry studied extensively by J. M. Lehn and co-workers.[15] Cryptates and cryptands are synthesized without the use of metal-ion template reactions using, instead, multistep organic syntheses which include high-dilution reactions. For most complexes of this type, the metal ions are highly labile and metal-exchange reactions occur facilely.

The second general type of clathrochelates characteristically have transition metal ions encapsulated by rigid ligand structures. For these complexes, the metal ions cannot be displaced by other metal ions or removed with the ligand remaining intact. Two general methods have been used to prepare these clathrochelates. In the more common method, a six-coordinate complex with purposefully functionalized ligands is treated with reagents which, through ring closure reactions with ligand functionalities, interconnect the ligands. Complexes prepared by this approach have been reported by Rose,[27] Holm,[28] Sargeson,[29] and Goedken.[30] The second method involves base-induced rearrangement of a metal-coordinated tetradentate ligand

which has a non-coordinated appendage containing additional donor atoms. Busch and co-workers have recently reported complexes prepared by this method.[31]

The MLH_3^{n+} and $M(II)M(II)L^+$ complexes described in this report have features in common with both types of clathrochelates described above including ligand flexibility and method of preparation. Comparing the former feature is relatively subjective owing to a lack of data for the previously reported complexes. Nevertheless, there is evidence which suggests that L^{3-} and LH_3 in $M(II)M(II)L^+$ and $M(II)LH_3^{2+}$ complexes, respectively, have some degree of rigidity comparable to the ligand flexibility of known rigid clathrochelates. In the case of L^{3-}, the ^1H NMR spectrum of $Cd(II)Cd(II)L^+$ at ambient temperatures exhibits resonances and couplings characteristic of a ligand structure with inflexible $-CH_2CH_2-$ subunits. From similar studies of $M(II)LH_3^{2+}$ complexes, the rigid nature of LH_3 is suggested by evidence for intramolecular hydrogen bonding. It is noteworthy, however, that the ligands in $M(II)M(II)L^+$ and $M(II)LH_3^{2+}$ complexes are not so inflexible that they cannot adopt slightly different geometries required for different metals. Indications for this adjustable rigidity are slight differences in the infrared spectra of these complexes (Table I) and by the anomalous basicity of $Cu(II)M(II)L^+$ complexes (M(II) = Cu and Zn). In contrast to the general ligand inflexibility of $M(II)LH_3^{2+}$ and $M(II)M(II)L^+$ complexes, the evidence for $NaLH_3NO_3$ strongly suggests ligand flexibility analogous to the cryptate/cryptand complexes. For these complexes, ligand flexibility is characterized by metal-ligand dissociative and/or internal site-site exchange processes occurring on the NMR time scale.

Preparative methods used for both general classes of clathrochelates discussed above are utilized in the syntheses of MLH_3^{n+} and $M(II)M(II)L^+$ complexes. Analogous to methods used for cryptate/cryptand complexes, $MLH_3^{2+,3+}$ complexes can be prepared by the direct substitution of an appropriate metal ion for a complexed alkalication (eq 5). Similarly, $M(II)M(II)L^+$ complexes can be synthesized by direct addition of a metal ion to a mononuclear clathrochelate with an available chelating site (eq 6). Analogous to the preparation of rigid clathrochelates, MLH_3^{n+} and $M(II)M(II)L^+$ complexes also can be prepared by reacting initially coordinated ligand constituents with other ligand components (eq 1, 3, and 4). In these reactions, tren is the ligand constituent which, in a quadridentate manner,[32] initially coordinates to a metal ion. As is invariably the case for known syntheses of rigid clathrochelates, subsequent clathrochelate-forming reactions of the initial complex are metal-ion specific.[27-31] As a result, MLH_3^{n+} and $M_A(II)M_B(II)L^+$ complexes have been prepared by rigid clathrochelate methods only for $M = Na^+$, Mn(II), Fe(II), Co(II), and Cd(II) and $M_A(II) = M_B(II) =$ Cd(II) and Mn(II).

The preparative methods for rigid clathrochelates described above can be included in a more general classification, metal-template reactions. Such reactions have been used extensively for preparing macrocyclic complexes[33] as well as clathrochelates. Although this classification is not normally subdivided, metal-template reactions are basically of two types: simple and complex. Simple metal-template reactions are characterized by ligand constituents which, if they are even capable of coordination, do not form initial complexes structurally

resembling the final product. Generally, such ligand constituents contribute at most three ligating atoms per metal to the final product. The preparation of phthalocyanine complexes from 1,2-dicyanobenzene and metal salts is an example of this simple metal-template reaction.[34] In contrast, complex metal-template reactions are characterized by one or more ligand constituents forming initial complexes which are structurally similar to the final product. In all cases, the coordinating ligand constituents are multidentate. The metal-ligand product results from ring closure reactions of non-coordinated ligand constituents with the coordinated ones. All of the preparations for previously reported rigid clathrochelates are examples of complex metal-template reactions.

In this regard, the metal-template reactions detailed here are exceptional in that the clathrochelates are formed by simple metal-template reactions. For example, in formation of the $M(II)LH_3^{2+}$ complexes, the tren is initially coordinated to the metal in a quadridentate manner (through its four nitrogen atoms); this ligand then undergoes a structural change in coordination geometry and is finally incorporated as a tridentate species. An even more remarkable example of a simple metal-template reaction is that which produces the Mn(II) and Cd(II) homonuclear complexes, $M(II)M(II)L^+$. In these cases, five ligand constituents are brought together around two metal ions to form a single, bicyclic ligand (>50% yield). The only literature example of a simple metal-template reaction which approaches the $M(II)M(II)L^+$ system in complexity is the formation of superphthalocyanine complexes from UO_2^{2+} and 5 equiv of 1,2-dicyanobenzene (<20% yield).[35]

Electrochemistry. Of the homobinuclear complexes ($M(II)M(II)L^+$) with electroactive metal ions, only $Fe(II)Fe(II)L^+$ shows two reversible, sequential redox processes, which in this case are oxidations. These redox processes are separated by an amount $\Delta E = 0.686V$, a quantity related thermodynamically to the comproportionation equilibrium as shown in eq. 7-10. Using eq 10, a $K_{com} = (4.0 \pm 0.1) \times 10^{11}$ can be

$$[Ox\text{-}Ox] + e^- \overset{E_1^f}{\rightleftharpoons} [Ox\text{-}Red] \tag{7}$$

$$[Ox\text{-}Red] + e^- \overset{E_2^f}{\rightleftharpoons} [Red\text{-}Red] \tag{8}$$

$$[Ox\text{-}Ox] + [Red\text{-}Red] \overset{K_{com}}{\rightleftharpoons} 2[Ox\text{-}Red] \tag{9}$$

$$E_1^f - E_2^f = \Delta E = (RT/nF) \ln K_{com} \tag{10}$$

calculated for $Fe(II)Fe(II)L^+$. Although both Cu(II)/Cu(I) reductions are not electrochemically reversible, a lower limit for a K_{com} of $Cu(II)Cu(II)L^+$ can be estimated as approximately 10^{13}. In comparison, the corresponding constant for Fe(II) and Cu(II) homobinuclear complexes of type 1 are 2.5×10^4 and 4.0×10^6, respectively.[1,36] For comparison with a system which is known to exhibit significant electronic delocalization, $(NH_3)_5Ru\text{-pyrazine-}Ru(NH_3)_5^{6+/5+/4+}$ has a reported $K_{com} = 4 \times 10^6$.[37]

Those interactions between metal centers which contribute significantly to a large ΔE, and thus a large K_{com}, are difficult to quantify, since K_{com} may reflect interactions which destabilize the [Ox-Ox] and [Red-Red] species and/or stabilize the [Ox-Red] species. Several

factors which affect the relative energetics of these three species have been cited previously[1] and are recounted briefly here: 1) Structural variations associated with oxidation state changes such as altered metal-ligand bonding distances and geometries are known to affect K_{com} values significantly.[38] 2) Electrostatic repulsion between proximate metal centers both through-orbital and through-space result in the addition of a second electron being energetically more difficult than the first process. 3) Electronic delocalization enhances the stability of the mixed-valent state with respect to the isovalent states. 4) Magnetic superexchange interactions are of potential significance for those oxidation states with coupled paramagnetic centers; however, for weakly coupled systems the net effect on K_{com} is usually negligible. 5) A statistical factor, which for totally non-interacting metal centers yields a $K_{com} = 4$ ($\Delta E = 36$ mV), contributes negligibly to K_{com} for systems for which the other factors affect K_{com} substantially.[1]

In a previous study, type $\underset{\sim}{1}$ complexes with M_A = Cu(II) and M_B = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II), were examined electrochemically and magnetically in an attempt to quantify some of the factors contributing to ΔE for the Cu(II) homonuclear complex.[1] The Cu(II)/Cu(I) reduction potentials were measured as a function of M_B and were found to be relatively invariant for $M_B \neq$ Cu(II). In contrast, E_1^f (which is the analogous potential for M_B = Cu(II)) is positive of the average heteronuclear value by 137 ± 14 mV, after minimal corrections were applied to account for magnetic superexchange. It was hypothesized that the average Cu(II)/Cu(I) reduction potential for the heteronuclear complexes was an accurate measure of E_1^f due only

to electrostatic repulsion. Based on this hypothesis, the 137 mV = 3.2 ± 0.3 kcal/mole difference between E_1^f (observed) and E_1^f (electrostatic repulsion only) was ascribed to electronic delocalization which stabilizes the mixed-valent Cu(II)-Cu(I) complex relative to the isovalent Cu(II)-Cu(II) complex.

For E_1^f (electrostatic repulsion only) to be accurately represented by the average Cu(II)/Cu(I) reduction potential of the heteronuclear complexes, two conditions must be satisfied. First, the mixed-valent heteronuclear complexes must be negligibly delocalized. Since these complexes have relatively inaccessible $M_B(II)/M_B(I)$ reduction potentials, this condition is met. Second, since electrostatic repulsion depends on the structural relationship between M_B and M_A, as M_A is reduced, structural differences between the homonuclear and heteronuclear complexes must be negligible or, at least, compensative. With the Cu(II)/Cu(I) reduction potentials being relatively insensitive towards M_B for $M_B \neq$ Cu(II), it is argued that structural differences in these complexes due to the nature of M_B are minimal. Assuming that this argument can be extended to M_B = Cu(II), the second condition is satisfied. It should be noted, however, that the axial ligand geometry of these complexes in solution is not rigorously controlled. Thus, it is conceivable that the homonuclear complex might be structurally anomalous with respect to the heteronuclear series. If this is the case, a reliable estimate cannot be obtained for the stabilization due to electronic delocalization.

The binuclear clathrochelate complexes, $M_A(II)M_B(II)L^+$, were examined to further evaluate the factors which contribute significantly

to ΔE, especially electrostatic repulsion and electronic delocalization. There were several reasons for studying complexes with this clathrochelating ligand, L^{3-}. First, such a ligand has the potential for rigorously controlling metal-ligand geometry and minimizing structural variations. Second, solvent and anion interactions with the cationic metal centers most likely would be hindered. Third, with three bridging atoms the magnitudes of the interactions between M_A and M_B might be greater than those of complexes with fewer bridging atoms. That some form of interaction between metals is enhanced in these complexes is strongly suggested by the exceptionally large ΔE values for $Fe(II)Fe(II)L^+$ and $Cu(II)Cu(II)L^+$.

To evaluate the principal contributions to ΔE for $M_A(II)M_B(II)L^+$ complexes, the same approach as in the study of type $\underset{\sim}{1}$ complexes was used. For three series of complexes, the potential of a M_A redox couple was determined as a function of a variable M_B. Specifically, the Mn(III)/Mn(II), Fe(III)/Fe(II) and Cu(II)/Cu(I) reduction potentials were measured, if observable, with respect to M_B = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Mg(II). The potentials were not adjusted to account for magnetic superexchange, since such interactions for these complexes are very weak. In contrast to the results observed for type $\underset{\sim}{1}$ Cu(II) heteronuclear complexes, the measured M_A redox potentials of $M_A(II)M_B(II)L^+$ complexes are not invariant with respect to M_B for $M_B \neq M_A$. The Fe(III)/Fe(II) and Cu(II)/Cu(I) reduction potentials, which have been determined for seven heteronuclear complexes, span ranges of 225 mV and 250 mV, respectively (Figure 9). The potential range of the less extensive

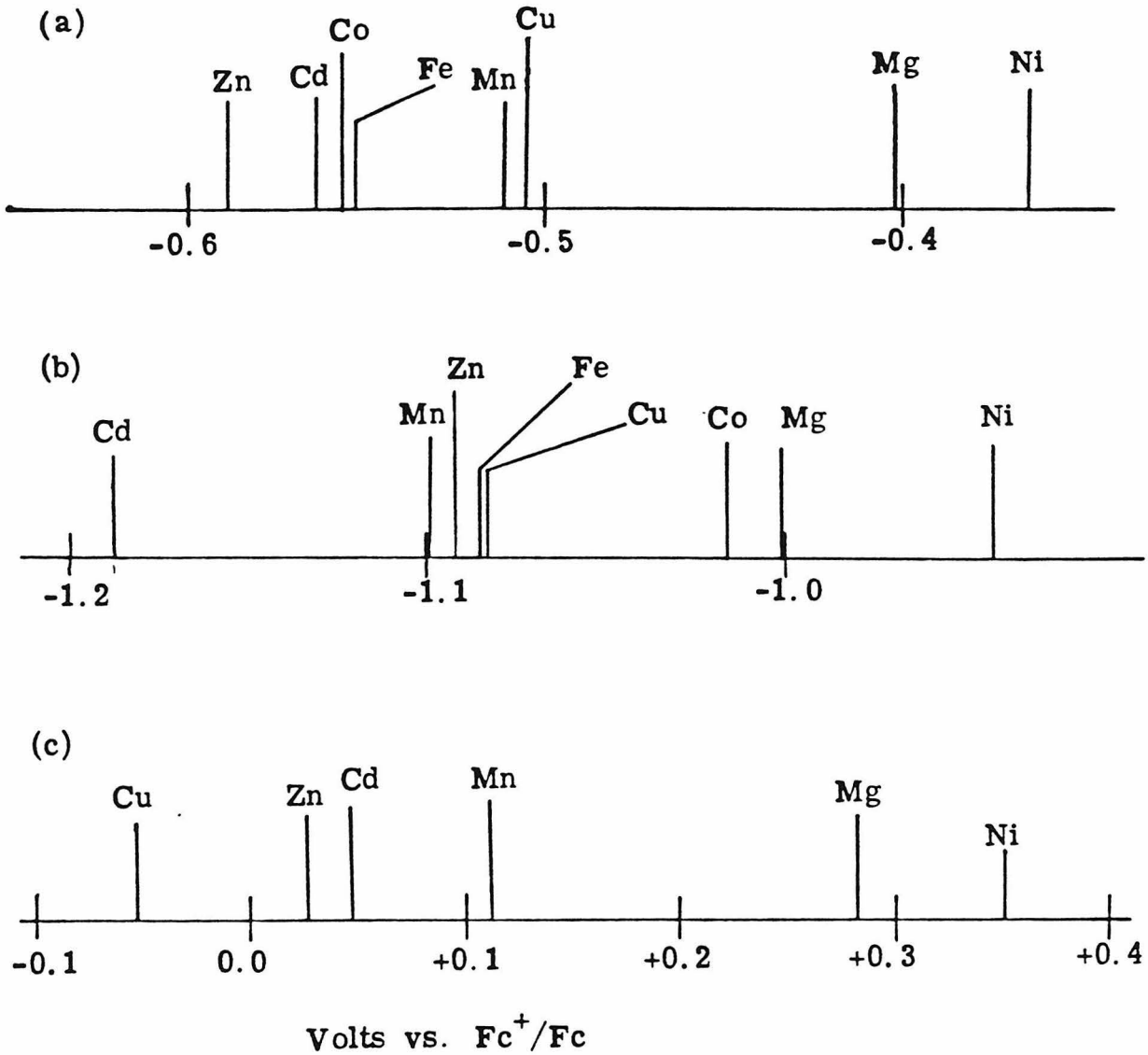


Figure 9. M_A Redox potentials in $M_A(II)M_B(II)L^+$ complexes as a function of M_B for (a) Fe(III)/(II) couple, (b) Cu(II)/(I) couple and (c) Mn(III)/(II) couple.

five-membered Mn(III)/Mn(II) series is 425 mV. In comparing the three series, the relative ordering of potentials from negative to positive appears to depend randomly on the nature of M_B, except for M_B = Ni(II) and Mg(II). For heteronuclear complexes containing these metals, the two most positive M_A redox potentials were consistently observed. If these systematically positive potentials are excluded from the Fe(III)/Fe(II) and Cu(II)/Cu(I) series, the range of potentials which depend non-systematically on the nature of M_B are reduced to 85 mV and 175 mV, respectively.

In spite of the considerable variance in the M_A redox potentials for $M_A(II)M_B(II)L^+$ complexes ($M_A \neq M_B$) described above, the data have been evaluated by the approach used in the study of type $\underset{\sim}{1}$ complexes. Specifically, the M_A potentials for a given series of $M_A(II)M_B(II)L^+$ heteronuclear complexes are averaged to give an estimated value of E_1^f or E_2^f due to electrostatic repulsion only. These estimated values are then compared with the corresponding observed E_1^f or E_2^f values. Using this approach on the restricted series of $Fe(II)M_B(II)L^+$ complexes ($M_B \neq$ Mg(II) or Ni(II)) yields E_2^f(electrostatic repulsion only) = -0.545 ± 0.036 V for comparison with E_2^f(observed) = -0.553 V. Similarly for the analogous series of $Cu(II)M_B(II)L^+$ complexes, a value for E_1^f(electrostatic repulsion only) = -1.096 ± 0.062 V is calculated for comparison with E_1^f(observed) = -1.083 V. If the M_B = Mg(II) and Ni(II) values are not excluded, E_2^f(electrostatic repulsion only) for $Fe(II)M_B(II)L^+$ is -0.499 ± 0.085 V, while E_1^f(electrostatic repulsion only) for $Cu(II)M_B(II)L^+$ is -1.060 ± 0.081 V. For the complete series of $Mn(II)M_B(II)L^+$ complexes,

a value for E_2^f(electrostatic repulsion only) = +0.136± 0.182 V is calculated for comparison with E_2^f(observed) = +0.114 V.

Two differences between these results and those for type $\underset{\sim}{1}$ complexes (M_A = Cu(II); M_B = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II)) are apparent. First, the uncertainties associated with the estimated values of E_1^f or E_2^f (electrostatic repulsion only) are considerable, since the M_A potentials for these $M_A(II)M_B(II)L^+$ complexes vary substantially. Second, there is no significant difference between E_1^f or E_2^f(electrostatic repulsion only) and E_1^f or E_2^f(observed) within the determined error limits. Provided this approach is valid, the apparent conclusion for these $M_A(II)M_B(II)L^+$ complexes is that there is negligible stabilization, within experimental error, for the mixed-valent homonuclear complexes relative to the analogous mixed-valent heteronuclear complexes. Specifically, for the restricted series of $Fe(II)M_B(II)L^+$ complexes, the stabilization of $Fe(III)Fe(II)L^{2+}$ relative to $Fe(III)M_B(II)L^{2+}$ ($M_B \neq$ Fe(II)) is 0.2± 0.8 kcal/mole. Similarly, for the restricted series of $Cu(II)M_B(II)L^+$ complexes, the stabilization of Cu(I)Cu(II)L relative to $Cu(I)M_B(II)L$ ($M_B \neq$ Cu(II) is 0.3± 1.4 kcal/mole. Using the complete data sets for $Fe(II)M_B(II)L^+$ and $Cu(II)M_B(II)L^+$ complexes gives stabilization values of 1.2± 2.0 kcal/mole and -0.5± 1.9 kcal/mole, respectively. For the less extensive $Mn(II)M_B(II)L^+$ series, the stabilization of $Mn(III)Mn(II)L^+$ relative to $Mn(III)M_B(II)L^+$ ($M_B \neq$ Mn(II)) is 0.5 ± 4.2 kcal/mole.

Before discussing factors which might account for the lack of stabilization for mixed-valent homonuclear complexes, the validity in

using the above approach for estimating the stabilization energies of these complexes should be considered. The approach is justifiable only if the average of the M_A redox potentials for a series of similar heteronuclear complexes provides a reasonable estimate for E_1^f or E_2^f (electrostatic repulsion only). The reasonableness of the estimate depends on 1) the mixed-valent heteronuclear complexes being negligibly electronically delocalized and 2) structural differences between the homonuclear and heteronuclear complexes being minimal. Condition 1 is satisfied since M_A and M_B redox potentials differ by at least 0.4 V in all of the $M_A(II)M_B(II)L^+$ complexes examined.

As has been discussed previously for type $\underset{\sim}{1}$ complexes, it is difficult to establish conclusively that the second condition is met. Based on structural studies of other clathrochelates in which only slight metal-dependent structural changes are observed,[13] it seems reasonable that homonuclear and heteronuclear $M_A(II)M_B(II)L^+$ complexes also will be structurally similar. Additionally, the near indistinguishability of infrared spectra for a given series of $M_A(II)M_B(II)L^+$ complexes is consistent with minimal structural differences. In apparent contradiction with these arguments, however, is the variability of redox potentials for a given series which suggests that structural differences in $M_A(II)M_B(II)L^+$ complexes might not be negligible. Although a degree of structural uncertainty has been introduced, it is still likely, based on the previous arguments, that a homonuclear complex will structurally resemble analogous heteronuclear complexes.

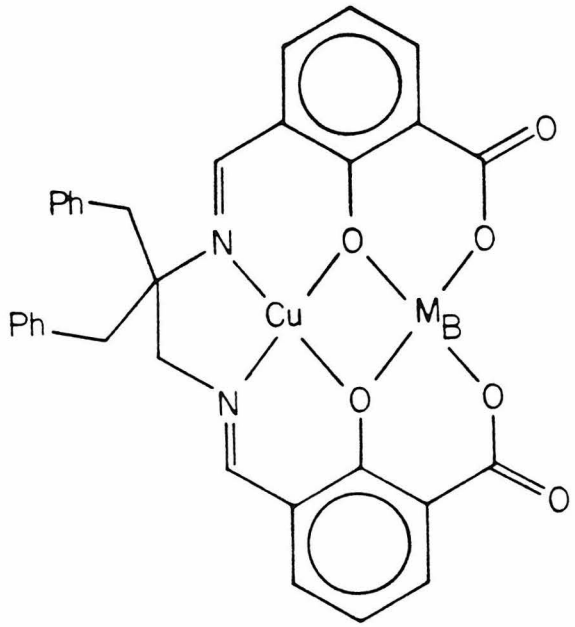
Owing to 1) the general structural similarities between $M(II)M(II)L^+$ (M = Fe and Cu) and type $\underset{\sim}{1}$ complexes and 2) the observation that large

K_{com} values often reflect a degree of electronic delocalization, it seemed reasonable that stabilization of mixed-valent states due to electronic delocalization for M(II)M(II)L^+ complexes might be of a measurable magnitude. Thus, it was surprising that the electrochemical results for both Fe(II)Fe(II)L^+ and Cu(II)Cu(II)L^+ complexes showed, within experimental error, no apparent stabilization of the mixed-valent states due to electronic delocalization. Plausible explanations for the lack of measurable stabilization include 1) the absence of metal-ligand orbital overlap of the appropriate magnitude or symmetry, 2) that even slight structural differences between M(II)M(II)L^+ complexes and type $\underset{\sim}{1}$ complexes might result in very different metal-metal communication, and 3) that these stabilization energies are inherently smaller than errors associated with the electrochemical method employed here. Independent magnetic studies yielded results consistent with the first explanation.

Results from other studies of electronic delocalization in binuclear complexes show very small, but measurable, stabilization energies consistent with the third explanation given above. By a method described by Taube et al.,[39] which avoids the necessity of preparing structurally similar homonuclear and heteronuclear complexes, electronic delocalization energies of Ru(II, III) dimers can be estimated. For $[((NH_3)_5Ru)_2$-(4, 4′-bipyridine)] and $(NH_3)_5$Ru(pyrazine)-Ru(edta)$^+$, these energies are 0.05[39] and 0.8 kcal/mole,[40] respectively. Both of these values are less than the uncertainty in the approach used to study M(II)M(II)L^+ complexes and the 0.05 kcal/mole values is less than the corresponding uncertainty for type $\underset{\sim}{1}$ complexes. Unfortunately,

neither M(II)M(II)L^+ nor type $\underset{\sim}{1}$ complexes are conducive to study by Taube's approach.

Since many complexes, including the M(II)M(II)L^+ series, cannot be studied by Taube's method, it is worth comparing and contrasting the results for known systems amenable to an electrochemical determination of delocalization energies. The complexes, $(NH_3)_5Ru(4,4'$-bipyridine)$Ru(NH_3)_5^{6+}$ and $(NH_3)_5Ru(4,4'$-bipyridine)$Rh(NH_3)^{6+}$, have Ru(III)/Ru(II) potentials of +0.79 V and +0.74 V, respectively.[41] In this case, the 50 mV (1.2 kcal/mole) potential difference has been ascribed to delocalization stabilization of the Ru(III)-Ru(II) mixed-valent complex.[1] A similar system, $(NH_3)_5Ru$(pyrazine)$Ru(edta)^+$ and $(NH_3)_5Ru$(pyrazine)$Rh(edta)^+$, has Ru(III)/Ru(II) potentials of -0.56 V and -0.61 V, respectively.[40] This result is counterintuitive since it suggests that the Ru(II)-Ru(III) mixed-valent complex is destabilized by 50 mV (1.2 kcal/mole) with respect to the Ru(II)-Rh(III) mixed-valent complex. This contrasting behavior is indicative of deficiencies in this electrochemical method for estimating a delocalization energy, especially when a <u>series</u> of structurally similar heteronuclear complexes are not examined. An interesting recent report details the electrochemistry of type $\underset{\sim}{3}$ complexes with M_B = Fe(II), Co(II), NI(II), Cu(II), Zn(II), Mg(II), Ca(II), and Ba(II).[42] These studies showed that the Cu(II)/Cu(I) reduction potential is invariant with respect to M_B for M_B = Fe(II), Co(II), Ni(II), Zn(II), and Mg(II), analogous to the behavior observed for type $\underset{\sim}{1}$ complexes. The surprising result of this study is that for M_B = Cu(II) the Cu(II)/Cu(I) potential is 480 mV



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positive of the average heteronuclear value. This 480 mV difference translates into an incredible 11 kcal/mole stabilization energy for the mixed-valent state, when, in fact, a negligible stabilization is expected for such an unsymmetrical complex.

In light of these above results, a reassessment of the validity of the electrochemical method for determining delocalization energies is warranted, especially in the cases of type 1 and 3 complexes. In the former case, there is additional experimental evidence which appears to contradict the interpretation of the measured stabilization as due to electronic delocalization. Specifically, CO binding studies for type 1 complexes (M_A = Cu(I) and M_B = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II)) indicate that CO binds most strongly to the mixed-valent Cu(II)-Cu(I) complex, and does so in a nonsymmetrical, terminal

fashion.[1,2] Bonding of CO to Cu(I) in the homonuclear system in an unsymmetrical fashion would certainly disrupt any delocalization and, thus, a preference for CO binding to Cu(I) in the homonuclear species should be disfavored with respect to binding to Cu(I) in the analogous heteronuclear species.

In the case of type $\underset{\sim}{3}$ complexes, single crystal X-ray structural results for similar complexes establish that the homonuclear complex (M_B = Cu(II)) is structurally different from heteronuclear analogues (M_B = Co(II) and Mg(II)).[43,44] These results are relevant to the electrochemical studies assuming that the solid-state structures are good representations of the solution structures. In the case of the homonuclear complex, the mean planes of the two four-coordinate sites intersect with a dihedral angle of 191.6°.[43] In contrast, the corresponding mean planes of the heteronuclear complexes intersect with a dihedral angle of 180°.[44] Although the difference is only $\sim 12°$, this increased twisting contributes to the shift of the Cu(II)/(I) potential (for the metal ion in N_2O_2 site) by 480 mV. It is noteworthy that arguments used in the electrochemical study of type $\underset{\sim}{1}$ complexes, based on the invariance of potentials for $M_B \neq$ Cu(II), would have suggested that structural differences between the homonuclear and heteronuclear complexes are negligible. It seems, therefore, impossible to predict whether there are important structural changes for these types of complexes in the absence of X-ray studies.

In light of the above considerations, it might be tempting to question the fundamental premise on which the electrochemical method for determining electronic delocalization is based, namely that

structural changes among a series of homonuclear and heteronuclear complexes is minimal. Certainly it appears treacherous to make any assumptions of isostructuralism for a series of complexes of types $\underset{\wedge}{1}$ and $\underset{\wedge}{3}$ (see above). However, since for $M(II)M(II)L^{+}$ complexes the same general results are observed for three different series (Fe, Cu, Mn), it is unlikely that the homonuclear species are uniformly structurally different with respect to their heteronuclear analogues. Thus, the application of the electrochemical method for these systems seems probably more valid than for the previously examined systems.

CONCLUSIONS

In an effort to study metal-metal communication in a clathrochelating environment, homonuclear and heteronuclear $M_A(II)M_B(II)L^+$ complexes of the ligand L^{3-}, a deprotonated Schiff-base compound derived from 3 equiv of 2-hydroxy-5-methylisophthalaldehyde and 2 equiv of 2,2',2"-triaminotriethylamine (tren), were synthesized and characterized. Two synthetic routes to these complexes were used. In the first method, a metal-ion specific template reaction, $Mn(II)Mn(II)L^+$ and $Cd(II)Cd(II)L^+$ were prepared directly from the reaction of 2 equiv of tren with 3 equiv of 2-hydroxy-5-methylisophthalaldehyde in the presence of Mn(II) or Cd(II) salts. In the second, more general method, a mononuclear complex of the non-deprotonated ligand, $NaLH_3NO_3$, was prepared by the condensation reaction of $\underset{\sim}{2}$ (a Schiff-base compound derived from 1 equiv of tren and 3 equiv of 2-hydroxy-5-methylisophthalaldehyde) with 1 equiv of both tren and $NaNO_3$. By using metathesis reactions, mononuclear $M(II)LH_3^{2+}$ complexes (M = Mn, Fe, Co, Ni, Cu, Zn, Cd, and Mg) were prepared from $NaLH_3NO_3$. Insertions of the same type of metal ion into $M(II)LH_3^{2+}$ complexes, in the presence of base, give the homonuclear $M(II)M(II)L^+$ products (M = Mn, Fe, Co, Cu, Zn, and Cd). By this method, the following heteronuclear complexes also have been prepared: $Mn(II)M(II)L^+$, $Fe(II)M(II)L^+$, and $Cu(II)M(II)L^+$ with M = Mn, Fe, Co, Ni, Cu, Zn, Cd, and Mg.

All homonuclear and heteronuclear $M_A(II)M_B(II)L^+$ complexes were examined by electrochemical methods (cyclic voltammetry and

differential pulse voltammetry). For the three series, the Mn(III)/Mn(II), Fe(III)/Fe(II), and Cu(II)/Cu(I) couples were determined as a function of adjacent metal ion. A comparison of the electrochemical results for these homonuclear and heteronuclear complexes shows that, within experimental error, there is no stabilization of the mixed-valent $Mn(III)Mn(II)L^{2+}$, $Fe(III)Fe(II)L^{2+}$, or Cu(I)Cu(II)L complexes with respect to mixed-valent heteronuclear analogues. These results are compared and contrasted with those obtained for other related binuclear systems.

EXPERIMENTAL SECTION

General Considerations. Unless noted otherwise, all solvents and reagents were purchased from commercial sources and were used without further purification. Tetrabutylammonium tetrafluoroborate, $TBABF_4$ (Southwestern Analytical Chemicals), was dried exhaustively in vacuo (25° C) before use. Reagent grade N, N-dimethylformamide, DMF, was dried over $MgSO_4$ and then doubly distilled under reduced pressure from activated 4-Å molecular sieves. 2-Hydroxy-5-methyl-isophthalaldehyde was prepared by a published modification[1] of the literature method.[45] It was purified by flash chromatography[46] on silica gel; the compound was loaded on and eluted from the column with toluene. The dialdehyde was isolated by precipitation with petroleum ether (30-60° C) from a concentrated solution of the eluate. 2, 2′, 2″-Triaminotriethylamine trihydrochloride, tren · 3HCl, prepared by the method of Kimura et al.,[47] was neutralized and distilled according to the procedure of Glerup et al.[48] to yield the free tetra-amine, tren. Preparation of air-sensitive compounds and the electrochemical experiments were carried out under helium in a Vacuum Atmospheres Dri-Lab inert atmosphere chamber.

Physical Measurements. ^1H NMR spectra were recorded with Varian EM390, JEOL FX90Q, or Bruker WM500 spectrometers. ^{13}C NMR spectra were obtained on a JEOL FX90Q spectrometer. Infrared spectra were recorded on a Beckman 4240 spectrometer. Samples were examined as KBr pellets.

Magnetic susceptibility measurements were obtained at ambient temperature using a Cahn Instruments Faraday balance. The

instrument was calibrated using $HgCo(SCN)_4$ and diamagnetic corrections were made using Pascal's constants.[49] Mössbauer data were collected on a previously described instrument.[50]

Elemental analyses were determined by Galbraith Laboratories, Inc.; the Spang Microanalytical Laboratory; and the California Institute of Technology's analytical facility.

Electrochemistry. Both a Princeton Applied Research (PAR) Model 174A polarographic analyzer and a PAR Model 173 potentiostat galvanostat coupled with a ramp generator of our own design were used for cyclic voltammetry. The PAR Model 174A was also utilized for differential pulse voltammetry. Results were displayed on either a Hewlett-Packard 7004B X-Y recorder or on a storage oscilloscope. Coulometric measurements were obtained by controlled potential electrolyses using the PAR Model 173 in conjunction with a PAR Model 179 digital coulometer.

For all electrochemical measurements the supporting electrolyte was 0.1 M $TBABF_4$ and a Ag^+/Ag reference electrode was used. The reference electrode consisted of a silver wire immersed in an acetonitrile solution containing $AgNO_3$ (0.01 M) and tetrabutylammonium perchlorate (0.1 M). The Ag^+ solution and silver wire were contained in an 8 mm glass tube fitted at one end with a fine porosity sintered glass frit. For the auxilliary electrode, either a coiled platinum wire or a compacted platinum gauze was used.

Cyclic and differential pulse voltammetry were carried out in a single compartment cell containing approximately 5 mL of solution. A platinum button electrode was used as a working electrode.

Controlled potential electrolyses were carried out in a three compartment H cell. The cell consisted of two 25 mL outer compartments connected to a 5 mL inner compartment by medium porosity sintered glass frits. A platinum gauze working electrode and the Ag^+/Ag reference electrode were situated in the outer compartment containing the electroactive solution. The auxilliary electrode was isolated in the other outer compartment.

By a method described elsewhere,[24] reduction potentials for the complexes were measured with respect to an internal standard which for most cases was ferrocene. When the ferricenium/ferrocene (Fc^+/Fc) wave overlapped with the wave under investigation, cobalticenium hexafluorophosphate was used; the cobalticenium/cobaltocene wave appears at -1.336 V vs. Fc^+/Fc. All potentials are reported versus the Fc^+/Fc couple.

Cd(II)Cd(II)LBF_4, Template Method. A warm solution of 133 mg (0.81 mmol) of 2-hydroxy-5-methylisophthalaldehyde and 8 drops of triethylamine (TEA) in 25 mL of ethanol was added dropwise to a warm, stirred solution of 137 mg (0.51 mmol) of tren in 25 mL of ethanol. The resulting yellow solution was heated at reflux for 20 min and then cooled to ambient temperature. A solution of 170 mg (0.51 mmol) of $TBABF_4$ in 5 mL of ethanol was added resulting in immediate precipitation of a lemon-yellow solid. The product (121 mg, 48%) was collected, washed with ethanol, washed with diethyl ether, and dried in vacuo.

Mn(II)Mn(II)LBF_4, Template Method. Under a helium atmosphere, a solution of 200 mg (0.82 mmol) of $Mn(OAc)_2 \cdot 4H_2O$ and

120 mg (0.82 mmol) of tren in 25 mL of ethanol was added dropwise to a warm, stirred solution of 210 mg (1.28 mmol) of 2-hydroxy-5-methylisophthalaldehyde and 8 drops of TEA in 25 mL of ethanol. The resulting yellow-orange solution was heated at reflux for 15 min. After the solution had cooled to ambient temperature, a solution of 140 mg (0.42 mmol) of $TBABF_4$ in 5 mL of ethanol was added. A yellow solid (0.21 g, 59%) precipitated immediately and was collected, washed with ethanol, washed with diethyl ether, and dried in vacuo.

3,3′,3″-Tris(2-hydroxybenzaldehyde-3-carboxaldimino)nitrilotriethane, (2). A slurry of 1.0 g (6.7 mmol) of 2-hydroxy-5-methylisophthalaldehyde in 5 mL of ethanol was stirred at 40° C until all the solid just dissolved. The heating was discontinued and ~10 mL of a solution of 0.2 g (1.4 mmol) of tren in 25 mL of ethanol was added dropwise to the stirred dialdehyde solution. The interior of the reaction flask was then scratched several times, and after stirring was resumed, yellow microcrystalline solid began to precipitate. To this stirred mixture, the remaining portion of the tren solution was added dropwise. After being cooled to ambient temperature, the mixture was filtered through a coarse frit. The collected solid (0.57 g, 70%) was washed with ethanol (2 × 10 mL) and diethyl ether (2 × 20 mL), and dried in vacuo.

^1H NMR ($CDCl_3$, chemical shifts, δ, in ppm relative to internal Me_4Si) 2.04 (3H, s, CH_3), 2.88 (2H, m, N-CH_2-R), 3.58 (2H, m, imine-CH_2-R), 6.39 and 7.54 (2H, d, aryl, J_{HH} = 2 Hz), 7.98 (1H, s, imine), and 10.05 (1H, s, aldehyde).

M(II)$LH_3(BF_4)_2 \cdot H_2O$ Template Method; M(II)=Mn(II), Fe(II), Co(II) and Cd(II). Preparations of Mn(II), Fe(II), and Co(II) complexes were conducted under a helium atmosphere. To a solution of 35 mg (0.24 mmol) of tren in 10 mL of ethanol was added 0.24 mmol of the appropriate hydrated metal(II) acetate and 10 mL of acetonitrile. The mixture was stirred until the metal salt dissolved and then added dropwise to a stirred slurry of 154 mg (0.26 mmol) of 2 in 15 mL of acetonitrile. After being stirred for 1 h, the resulting solution was filtered, and a solution of 238 mg (0.72 mmol) of $TBABF_4$ in 30 mL of ethanol was added. If solid precipitated, acetonitrile was added dropwise until the solid just dissolved. Slow evaporation of the solution over a period of 4-5 days resulted in the product crystallizing from solution. The crystals (30-50% yield) were collected, washed with ethanol, washed with diethyl ether, and air dried. The colors of the complexes are as follows: Mn(II) orange-yellow, Fe(II) green, Co(II) yellow-orange, and Cd(II) yellow.

$NaLH_3NO_3$. A mixture of 87.7 mg (0.60 mmol) of tren and 51.0 mg (0.60 mmol) of sodium nitrate in ethanol (23 mL) and acetonitrile (15 mL) was stirred until all of the sodium nitrate dissolved. This solution was added to a stirred slurry of 370 mg (0.63 mmol) of 2 in 25 mL of acetonitrile. The resulting yellow solution was stirred for 1 h, filtered, and diluted with 40 mL of ethanol. After reducing the solution volume to 25 mL using a rotary evaporator, 30 mL of diethyl ether was added. Yellow microcrystalline needles formed immediately which upon standing overnight recrystallized as orange-yellow parallelepipeds (380 mg, 83%). The product was collected, washed with

diethyl ether, and dried in vacuo.

M(II)$LH_3(BF_4)_2 \cdot H_2O$ Exchange Method; M=Mn(II), Fe(II), Co(II), Ni(II), Zn(II), Cd(II), and Mg(II). For all metals except Fe(II), a solution of 0.36 mmol of the appropriate hydrated metal(II) acetate in 20 mL of methanol was prepared. For Fe(II), 0.36 mmol of $FeCl_2 \cdot 2THF$[51] was used instead. The metal solution was added dropwise to a stirred solution of 305 mg (0.40 mmol) of $NaLH_3NO_3$ in 40 mL of methanol. The solution was stirred for 15 min and then filtered. To the stirred filtrate was added a solution of 500 mg (1.5 mmol) of $TBABF_4$ in 20 mL of methanol. Solid precipitated and was collected, washed with 1:1 methanol/diethyl ether (2 × 15 mL) and diethyl ether (2 × 20 mL), and dried in vacuo. Yields of complexes were generally greater than 85%. The colors of those complexes which can be prepared only by this method are as follows: Ni(II) gold, Zn(II) yellow, and Mg(II) yellow.

Cu(II)$LH_3(BF_4)_2 \cdot 3/2H_2O$. To a stirred slurry of 600 mg (0.79 mmol) of $NaLH_3NO_3$ in 60 mL of methanol was added 125 mg (0.63 mmol) of $Cu(OAc)_2 \cdot H_2O$. The resulting brown solution was stirred for 15 min and then filtered. To the stirred filtrate was added a solution of 1.0 g (3.0 mmol) of $TBABF_4$ in 15 mL of methanol. A gold-brown solid (210 mg, 35%) crystallized which was collected, washed with 1:1 methanol/diethyl ether, and dried in vacuo.

Fe(III)$LH_3(BF_4)_3$. To a slurry of 400 mg (0.53 mmol) of $NaLH_3NO_3$ in 80 mL of methanol was added a solution of 216 mg (0.80 mmol) of $FeCl_3 \cdot 6H_2O$ in 15 mL of methanol. After being stirred for 15 min, the resulting dark-blue solution was filtered. To the

filtrate was added 1.5 g (4.5 mmol) of $TBABF_4$. The volume of the solution was reduced to 10 mL using a rotary evaporator. The dark-blue solid (380 mg, 72%) which crystallized from the solution was collected, washed with methanol, washed with diethyl ether, and dried in vacuo.

$MnLH_3(ClO_4)_3$. Under a helium atmosphere, a solution of 110 mg (0.12 mmol) of $Mn(II)LH_3(BF_4)_2 \cdot H_2O$ in 30 mL of acetonitrile (0.1 M in tetrabutylammonium perchlorate) was electrolyzed at 0.7 V vs. a Ag^+/Ag reference electrode. After passing 12.1 coulombs, a solution of 1.0 g (2.9 mmol) of tetrabutylammonium perchlorate in 75 mL of methanol was added to the electrolytic solution. Using a rotary evaporator, the volume of the solution was reduced to 15 mL resulting in the crystallization of a dark-brown solid. The product (66 mg, 55%) was collected, washed with methanol, washed with diethyl ether, and dried in vacuo.

$Fe(II)Fe(II)LBF_4$. Under a helium atmosphere, a solution of 150 mg (0.86 mmol) of $Fe(OAc)_2$ in 20 mL of warm methanol was added to a solution of 300 mg (0.39 mmol) of $NaLH_3NO_3$ in 50 mL of methanol. After being stirred for 15 min, the solution was filtered and 8 drops of TEA was added. The solution was warmed to 50° C and stirred for 15 min. After being cooled to ambient temperature, the solution was stirred for an additional 12 h. A small amount of microcrystalline $Fe(II)Fe(II)LNO_3$ was removed by filtration, and a solution of 300 mg (0.91 mmol) of $TBABF_4$ in 15 mL of methanol was added to the filtrate. A brown, microcrystalline solid (192 mg, 56%) was collected, washed with methanol, washed with diethyl ether, and dried under a stream of helium.

Co(II)Co(II)LBF$_4$ · H$_2$O. Under a helium atmosphere, 8 drops of TEA and a filtered solution of 87 mg (0.35 mmol) of Co(OAc)$_2$ · 4H$_2$O in 20 mL of methanol were added to a filtered solution of 300 mg (0.32 mmol) of Co(II)LH$_3$(BF$_4$)$_2$ · H$_2$O in 70 mL of 1:1 methanol/acetonitrile. The solution was stirred for 12 h during which time an orange solid precipitated. The solid (198 mg, 69%) was collected, washed with 1:1 methanol/acetonitrile (2 × 20 mL) and diethyl ether (2 × 20 mL), and dried in vacuo.

Cu(II)Cu(II)LBF$_4$ · 2H$_2$O. To a stirred solution of 300 mg (0.39 mmol) of NaLH$_3$NO$_3$ in 80 mL of methanol was added 173 mg (0.87 mmol) of Cu(OAc)$_2$ · H$_2$O. The resulting green solution was filtered, and 400 mg (1.2 mmol) of TBABF$_4$ was added to the filtrate. The volume of the solution was reduced to 20 mL using a rotary evaporator. A dark-green solid crystallized from the solution and was collected, washed with 1:1 methanol/diethyl ether, and dried in vacuo.

Cu(II)Cu(II)LBF$_4$ · H$_2$O. To a solution of 325 mg (0.33 mmol) of Cu(II)Cu(II)LH(BF$_4$)$_2$ · 2H$_2$O in 30 mL of acetonitrile was added 3 mL of diisopropylethylamine and 80 mL of methanol. The resulting orange-red solution was concentrated to a volume of 15-20 mL using a rotary evaporator. Upon standing for 4-6 h, the solution yielded maroon-red crystals (136 mg, 45%). This hygroscopic product was collected, washed with 100:1 methanol/diisopropylethylamine (2 × 20 mL) and diethyl ether (2 × 25 mL), and dried in vacuo.

M$_A$(II)M$_B$(II)LBF$_4$ · xH$_2$O Insertion of M$_B$(II) into M$_A$(II)LH$_3$(BF$_4$)$_2$ · xH$_2$O; General Method. The following general method can be used to prepare most of the homonuclear and heteronuclear M$_A$(II)M$_B$(II)L$^+$

complexes. Specific details are reported following the general procedure for those complexes which were prepared by this method.

If either M_A(II) or M_B(II) was Mn, Fe, or Co, the preparation was carried out under a helium atmosphere. A filtered solution of 0.49 mmol of M_B(II) acetate (hydrate except for Fe(II)) in 25 mL of methanol (heated to 50° C for Fe(II)) and 8 drops of TEA were added to a filtered solution of 0.49 mmol of $M_A(II)LH_3(BF_4)_2 \cdot xH_2O$ in acetonitrile (30-35 mL) and methanol (40-45 mL). While the solution was being stirred for 12 h, a microcrystalline solid precipitated. The product was collected, washed with methanol (2 × 20 mL) and diethyl ether (2 × 20 mL), and dried in vacuo.

Mn(II)M(II)LBF$_4$ M = Mn(II) and Co(II). The mononuclear complex into which Mn(II) and Co(II) were inserted was $Mn(II)LH_3(BF_4)_2 \cdot H_2O$. Yellow Mn(II)Mn(II)LBF$_4$ and orange Mn(II)Co(II)LBF$_4$ were isolated in 65-70% yields.

Fe(II)M(II)LBF$_4$ M = Mn(II), Co(II), and Cu(II). The mononuclear complex into which Mn(II), Co(II), and Cu(II) were inserted was $Fe(II)LH_3(BF_4) \cdot H_2O$. Dark-green Fe(II)Mn(II)LBF$_4$, brown Fe(II)Co(II)LBF$_4$, and black Fe(II)Cu(II)LBF$_4$ were isolated in 50-65% yields.

M(II)Ni(II)LBF$_4$ M = Mn(II) and Fe(II). The mononuclear complex into which Mn(II) and Fe(II) were inserted was $Ni(II)LH_3(BF_4)_2 \cdot H_2O$. Light-brown Ni(II)Mn(II)LBF$_4$ and red-brown Ni(II)Fe(II)LBF$_4$ were isolated in 60-70% yields.

Cu(II)M(II)LBF$_4 \cdot xH_2O$ M = Mn(II) and Co(II). The mononuclear complex into which Mn(II) and Co(II) were inserted was

$Cu(II)LH_3(BF_4)_2 \cdot 3/2H_2O$. Orange-brown $Cu(II)Mn(II)LBF_4 \cdot H_2O$ and brown $Cu(II)Co(II)LBF_4 \cdot \frac{1}{2}H_2O$ were isolated in 65-70% yields.

M(II)Zn(II)$LBF_4 \cdot xH_2O$ M=Mn(II), Fe(II), and Zn(II). The mononuclear complex into which Mn(II), Fe(II), and Zn(II) were inserted was $Zn(II)LH_3(BF_4)_2 \cdot H_2O$. A second crop of $Mn(II)Zn(II)LBF_4$ was isolated from the filtrate after the volume had been reduced to ~30 mL using a rotary evaporator. Yellow $Mn(II)Zn(II)LBF_4$, brown $Fe(II)Zn(II)LBF_4 \cdot H_2O$, and yellow $Zn(II)Zn(II)LBF_4$ were isolated in 70-85% yield.

M(II)Cd(II)LBF_4 M=Mn(II), Fe(II), Cu(II), and Cd(II). The mononuclear complex into which Mn(II), Fe(II), Cu(II), and Cd(II) were inserted was $Cd(II)LH_3(BF_4)_2 \cdot H_2O$. A second crop of $Cd(II)Cd(II)LBF_4$ was isolated from the filtrate after the volume had been reduced to ~20 mL using a rotary evaporator. Yellow $Mn(II)Cd(II)LBF_4$, brown $Fe(II)Cd(II)LBF_4$, light orange-brown $Cu(II)Cd(II)LBF_4$, and light yellow $Cd(II)Cd(II)LBF_4$ were isolated in 75-85% yields.

M(II)Mg(II)LBF_4; M=Mn(II), Fe(II). The mononuclear complex into which Mn(II) and Fe(II) were inserted was $Mg(II)LH_3(BF_4)_2 \cdot H_2O$. Yellow $Mn(II)Mg(II)LBF_4$ and light maroon $Fe(II)Mg(II)LBF_4$ were isolated in 55-65% yields.

Cu(II)M(II)LBF_4; M=Ni(II), Mg(II). To a filtered solution of 450 mg (0.48 mmol) of $Cu(II)LH_3(BF_4)_2 \cdot 3/2H_2O$ in acetonitrile (30 mL) and methanol (55 mL) were added 8 drops of TEA and a filtered solution of 0.49 mmol of the appropriate hydrated metal(II) acetate in 25 mL of methanol. The solution was stirred for 2 h and then 25 mL of methanol was added. The solution was concentrated to 15 mL using a rotary evaporator. The brown microcrystals (40-55% yield) which

had formed were collected, washed with 2:1 methanol/diethyl ether (2 × 20 mL) and diethyl ether (2 × 20 mL), and dried in vacuo.

Cu(II)Zn(II)LBF$_4$ · H$_2$O. To a filtered solution of 300 mg (0.32 mmol) of Cu(II)LH$_3$(BF$_4$)$_2$ · 3/2H$_2$O in acetonitrile (25 mL) and methanol (35 mL) was added a filtered solution of 70 mg (0.32 mmol) of Zn(OAc)$_2$ · 2H$_2$O in 35 mL of methanol. After adding 2 mL of diisopropylethylamine) the solution was concentrated to 15-20 mL using a rotary evaporator. Upon standing for 4-6 h, the solution yielded red-brown crystals (121 mg, 42%). The product was collected, washed with 100:1 methanol/diisopropylethylamine (2 × 20 mL) and diethyl ether (2 × 25 mL), and dried in vacuo.

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CHAPTER 3

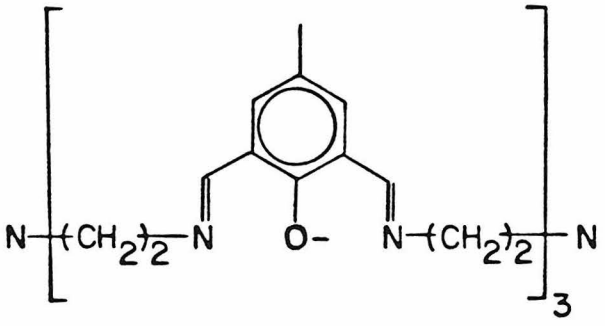
Magnetic Properties of Binuclear Clathrochelate Complexes

INTRODUCTION

Binuclear complexes with magnetically interacting metal centers have been examined in efforts (1) to understand the mechanisms of spin-spin coupling[1-3] and (2) to develop model systems for magnetic interactions in linear chains, clusters, and paramagnetic aggregates. Certainly the most extensively studied series of such binuclear complexes are those with Cu(II) metal centers and two bridging oxygen-donor ligands.[4-6] From these studies a theoretical relationship between J-values and metal-ligand-metal bridging angle has been developed.[6b]

Two general classes of magnetically interacting binuclear complexes which have received less attention are (1) those with three symmetrically bridging ligands[7,8] and (2) those in which the metal ions are varied systematically.[9-11] Such studies of the latter type are essential for obtaining an understanding of the relationships between exchange coupling and the number of unpaired electrons. These studies have been limited because of the difficulty in preparing structurally similar complexes for a series of different metal ions.

The general syntheses of binuclear complexes of the clathrochelating ligand, L^{3-}, allow the examination of magnetic interactions



L^{3-}

for several different pairs of metal ions. In complexes of L^{3-} the metal ions are likely to be symmetrically bridged by three phenolic oxygens. Although metal-ligand geometry may differ depending on the nature of the metals, a clathrochelating ligand is likely to minimize these structural variations. The results of variable-temperature magnetic susceptibility studies for a series of four of these complexes are reported here.

RESULTS

Variable temperature (4.2 to > 220 K) magnetic susceptibility data were collected for Mn(II)Mn(II)LBF_4, Fe(II)Fe(II)LBF_4, Co(II)Co(II)$LBF_4 \cdot H_2O$, and Cu(II)Cu(II)$LBF_4 \cdot H_2O$. For each set of data a least-squares fit to an appropriate equation was calculated. These equations include a theoretical expression (from Van Vleck's equation) derived for isotropic exchange interactions ($H = -2JS_1 \cdot S_2$) and a correction term for paramagnetic impurities (PARA); details are given in the Experimental Section. Both data and least-square results for the complexes are given in Tables I-IV and are depicted graphically in Figure 1-4.

The molar susceptibility (χ) for Mn(II)Mn(II)LBF_4 as a function of temperature (T) does not appear to differ significantly from Curie-law behavior (Figure 1). There are, however, two obvious indications for an antiferromagnetic interaction in this complex. First, the effective moment per metal ion (μ_{eff}/Mn) at ambient temperature, 5.6(1) μ_B, is lower than the expected spin-only value ($S_1 = S_2 = 5/2$) of 5.92 μ_B. Second, μ_{eff}/Mn decreases significantly from 5.51 μ_B at 224 K to 1.62 at 4.2 K (Table I). The least-squares fitting of the data gives

values indicating weak antiferromagnetic coupling with $J = -2.8\ cm^{-1}$, $g = 1.94$, and PARA = 0.0961 cgsu. A likely impurity, which would necessitate a paramagnetic correction, is $Mn(II)LH_3(BF_4)_2 \cdot H_2O$.

The χ vs. T curve for $Fe(II)Fe(II)LBF_4$ more closely resembles an ideal Curie-law χ vs. T curve than that of $Mn(II)Mn(II)LBF_4$ (Figure 2). Indeed, prior to a least-squares fitting of the data, the only evidence for a magnetic interaction is the substantial decrease of μ_{eff}/Fe from 5.58 μ_B at 286 K to 3.12 μ_B at 4.2 K (Table II). This behavior is consistent with weak antiferromagnetic coupling, and is supported by a least-squares fitting of the data which gives $J = -0.82\ cm^{-1}$ and $g = 2.22$. There is no evidence for paramagnetic impurities since PARA = 0.00.

The behavior of χ as a function of T for $Co(II)Co(II)LBF_4 \cdot H_2O$ is very similar to that for $Fe(II)Fe(II)LBF_4$ (Figure 3). Weak antiferromagnetic coupling again is suggested by the decrease of μ_{eff}/Co from 4.81 μ_B at 286 K to 3.54 μ_B at 4.2 K (Table III). Values for J and g of $0.93\ cm^{-1}$ and 2.49, respectively, have been obtained from a least-squares fitting of the data. As was the case for samples of $Fe(II)Fe(II)LBF_4$, those of $Co(II)Co(II)LBF_4 \cdot H_2O$ were not contaminated by paramagnetic impurities (PARA = 0.00).

Of the four clathrochelates examined by variable temperature magnetic techniques, only $Cu(II)Cu(II)LBF_4 \cdot H_2O$ has a maximum molar susceptibility at an intermediate temperature ($\sim$ 65 K) characteristic of an antiferromagnetic interaction (Figure 4). Additionally, μ_{eff}/Cu decreases from 1.83 μ_B at 245 K to 0.20 μ_B at 4.84 K (Table IV). A least-squares fitting of the data gives $J = -33.5\ cm^{-1}$, $g = 2.19$, and

PARA = 0.0418 cgsu. Possible paramagnetic impurities are mononuclear Cu(II) species.

DISCUSSION

The magnetic exchange parameters (J-values) for the four binuclear clathrochelate complexes are summarized in Table V. The data indicate that the metals in all four complexes are weakly antiferromagnetically coupled.

For certain geometries and d-electron configurations, weak antiferromagnetic interactions can result from the cancellation of considerable antiferromagnetic interactions by roughly compensatory ferromagnetic interactions.[12] Since the weak interactions in these $M(II)M(II)L^+$ complexes are generally independent of the spin state of M(II), an alternative explanation for these weak interactions must be invoked. A reasonable explanation for these interactions is that the overlap of metal d-orbitals with the s- and p-orbitals of the bridging phenolic oxygens is small.[13] Structural studies which are in progress should clarify the nature of the metal-oxygen bonds in these complexes.

There are few related first-row transition-metal complexes having three bridging ligands with which to compare the results obtained for the $M(II)M(II)L^+$ complexes reported here. Several $[M(III)_2Cl_9]^{3-}$ complexes with three bridging chloride ligands have been observed to exhibit weak antiferromagnetic interactions ($-25\ cm^{-1} < J < -1\ cm^{-1}$).[7] In a few of these cases, the weak couplings also have been ascribed to poor orbital overlap.[7ab] However, since both metal ion charges and bridging ligands differ from those of $M(II)M(II)L^+$ complexes, these results are not comparable. It is clear

that additional studies are needed to unambiguously define the nature of these weak interactions.

Experimental Section

All compounds were prepared and characterized as described in Chapter 2. A PAR Model 150A vibrating sample magnetometer operated at 13.5 KG was used to obtain the variable-temperature susceptibility data. The instrument was standardized with respect to $CuSO_4 \cdot 5H_2O$ in the temperature range, 4.2-286 K, using the reported molar susceptibility values.[14] Sample temperature was determined using a calibrated GaAs diode. The data for all samples and at all temperatures were corrected for the diamagnetism of the sample container and the background. Additionally, the data were corrected for diamagnetism of each compound using estimated values from Pascal's constants.[15]

The resulting paramagnetic susceptibility data were least squares fit, using an available computer program,[16] to the appropriate equations which include a theoretical expression and a correction term for paramagnetic impurities. The theoretical expressions are based on a spin Hamiltonian for isotropic magnetic exchange, $H = -2JS_1 \cdot S_2$. The general form for these expressions is given in eq 1 as has been reported by Earnshaw et al.[17] All of the constants have their usual

$$\chi_M = (Ng^2\beta^2/3kT)\{\sum_{S'} S'(S'+1)(2S'+1)\Omega(S')_{exp}(-E_{S'}/kT)\}/$$
$$\{\sum_{S'} (2S'+1)\Omega(S')_{exp}(E_{S'}/kT)\} \qquad (1)$$

meanings. For homonuclear complexes S is defined as $S_1 = S_2$. The term, S', is the quantum number of the coupled energy levels and assumes values of $2S, 2S-1, 2S-2, \ldots, 0$ in the summation. The

energy term, $E_{S'}$, is equal to $-J[S'(S'+1) - 2S(S+1)]$, and $\Omega(S')$ is the degeneracy of a given energy level. The variable term for paramagnetic impurities is included in the appropriate equations as $(4.2/T)$ PARA.

Table I. Experimental and Calculated Magnetic Susceptibility Data for Mn(II)Mn(II)LBF$_4$

T, °K	$\chi_M \times 10^1$, cgsu		μ_{eff}/Mn, μ_B	
	obsd	calcd	obsd	calcd
224.	0.3389	0.3472	5.51	5.58
203.	0.3727	0.3778	5.51	5.55
183.	0.4055	0.4143	5.45	5.51
163.	0.4496	0.4584	5.41	5.46
143.	0.5023	0.5119	5.35	5.40
122.	0.6063	0.5784	5.45	5.32
103.	0.6701	0.6816	5.25	5.21
94.2	0.6974	0.7051	5.12	5.15
86.6	0.7351	0.7480	5.04	5.09
76.9	0.7532	0.8098	4.81	4.99
67.0	0.8582	0.8820	4.80	4.86
61.6	0.9056	0.9255	4.72	4.77
55.9	0.9479	0.9746	4.60	4.67
45.2	1.024	1.074	4.30	4.41
41.9	1.056	1.106	4.21	4.30
38.6	1.086	1.138	4.10	4.19
35.3	1.120	1.169	3.98	4.06
32.0	1.156	1.199	3.85	3.92
28.1	1.208	1.253	3.68	3.72
24.2	1.262	1.264	3.49	3.50
22.2	1.290	1.280	3.38	3.37

Table I (continued)

21.2	1.298	1.287	3.32	3.30
20.2	1.303	1.295	3.24	3.23
18.9	1.312	1.305	3.15	3.14
17.7	1.322	1.316	3.06	3.05
16.1	1.345	1.330	2.94	2.92
14.5	1.369	1.347	2.82	2.79
12.6	1.411	1.373	2.66	2.62
10.6	1.464	1.408	2.49	2.44
10.2	1.476	1.418	2.45	2.40
9.71	1.488	1.429	2.40	2.36
9.38	1.502	1.437	2.37	2.32
8.95	1.519	1.449	2.33	2.28
8.44	1.537	1.465	2.28	2.22
7.77	1.562	1.489	2.20	2.15
7.29	1.589	1.508	2.15	2.10
6.32	1.612	1.556	2.02	1.98
5.64	1.626	1.598	1.91	1.90
5.24	1.665	1.628	1.87	1.85
4.46	1.550	1.697	1.66	1.74
4.20	1.573	1.725	1.62	1.70

Table II. Experimental and Calculated Magnetic Susceptibility Data for Fe(II)Fe(II)LBF$_4$

T, °K	$\chi_M \times 10^1$, cgsu		μ_{eff}/Fe, μ_B	
	obsd	calcd	obsd	calcd
286.	0.2724	0.2547	5.58	5.39
265.	0.2806	0.2740	5.45	5.39
745.	0.2980	0.2964	5.40	5.38
224.	0.3207	0.3229	5.36	5.38
204.	0.3620	0.3546	5.43	5.37
183.	0.4252	0.3931	5.58	5.36
163.	0.4566	0.4410	5.45	5.35
143.	0.5113	0.5012	5.41	5.35
123.	0.5927	0.5803	5.39	5.33
103.	0.6923	0.6861	5.33	5.31
94.2	0.7585	0.7455	5.34	5.30
86.1	0.8072	0.8115	5.27	5.28
76.9	0.8985	0.9023	5.26	5.27
67.0	1.018	1.026	5.22	5.24
61.4	1.098	1.110	5.19	5.22
55.9	1.194	1.210	5.17	5.20
51.4	1.273	1.305	5.12	5.18
43.3	1.470	1.521	5.04	5.13
39.8	1.583	1.638	5.02	5.10
36.2	1.700	1.773	4.96	5.07
32.8	1.839	1.931	4.91	5.03

Table II (continued)

29.3	2.011	2.119	4.85	4.98
25.6	2.198	2.354	4.75	4.91
22.0	2.457	2.644	4.65	4.82
20.2	2.618	2.814	4.60	4.77
19.6	2.706	2.884	4.59	4.74
18.8	2.819	2.958	4.50	4.72
17.0	2.961	3.158	4.49	4.64
15.3	3.126	3.362	4.37	4.55
13.7	3.205	3.601	4.26	4.45
12.2	3.295	3.857	4.08	4.32
10.1	3.979	4.176	4.00	4.10
7.73	4.534	4.530	3.74	3.74
7.14	4.543	4.603	3.60	3.62
6.55	4.639	4.665	3.49	3.50
5.96	4.742	4.709	3.36	3.35
5.38	4.872	4.733	3.24	3.19
4.79	5.109	4.732	3.13	3.01
4.49	5.364	4.720	3.10	2.91
4.20	5.799	4.701	3.12	2.81

Table III. Experimental and Calculated Magnetic Susceptibility Data for $Co(II)Co(II)LBF_4 \cdot H_2O$

T, °K	$\chi_M \times 10^1$, cgsu		μ_{eff}/Co, μ_B	
	obsd	calcd	obsd	calcd
286.	0.2024	0.2008	4.81	4.79
265.	0.2175	0.2161	4.80	4.78
245.	0.2305	0.2339	4.83	4 78
224.	0.2603	0.2547	4.83	4.78
204.	0.2863	0.2800	4.83	4.78
183.	0.3181	0.3107	4.83	4.77
163.	0.3555	0.3489	4.81	4.77
143.	0.4051	0.3970	4.81	4.76
122.	0.4519	0.4605	4.70	4.75
103.	0.5487	0.5458	4.75	4.74
94.2	0.6047	0.5938	4.77	4.73
86.1	0.6438	0.6474	4.70	4.72
76.9	0.7093	0.7213	4.67	4.71
67.0	0.8050	0.8222	4.64	4.69
61.6	0.8661	0.8901	4.62	4.68
55.9	0.9484	0.9751	4.60	4.67
50.2	1.046	1.078	4.58	4.65
47.5	1.103	1.135	4.58	4.64
44.8	1.166	1.198	4.57	4.63
41.8	1.241	1.276	4.55	4.62
38.8	1.319	1.364	4.53	4.60

Table III (continued)

35.3	1.426	1.485	4.49	4.58
31.9	1.567	1.626	4.47	4.56
28.6	1.721	1.788	4.44	4.52
24.9	1.919	2.012	4.37	4.48
22.8	2.065	2.168	4.34	4.44
21.6	2.152	2.263	4.31	4.42
20.5	2.249	2.365	4.29	4.40
17.8	2.513	2.641	4.23	4.34
15.0	2.667	2.994	4.15	4.24
13.2	3.135	3.281	4.07	4.16
11.1	3.526	3.601	3.96	4.04
10.7	3.631	3.751	3.94	4.00
10.2	3.711	3.841	3.90	3.97
10.0	3.755	3.888	3.88	3.95
9.81	3.784	3.935	3.85	3.93
9.59	3.839	3.984	3.84	3.91
9.38	3.883	4.030	3.82	3.89
9.16	3.964	4.080	3.81	3.86
8.94	4.005	4.130	3.78	3.84
8.74	4.057	4.176	3.77	3.82
8.54	4.110	4.223	3.75	3.80
8.35	4.180	4.267	3.74	3.77
7.95	4.279	4.368	3.67	3.72
7.55	4.421	4.454	3.65	3.67

Table III (continued)

7.18	4.543	4.545	3.61	3.61
6.78	4.670	4.635	3.55	3.54
6.37	4,842	4.720	3.51	3.47
5.71	4.993	4.851	3.38	3.33
5.12	5.301	4.944	3.29	3.18
4.20	5.464	5.017	3.54	2.98

Table IV. Experimental and Calculated Magnetic Susceptibility Data for $Cu(II)Cu(II)LBF_4 \cdot H_2O$

T, °K	$\chi_M \times 10^1$, cgsu		μ_{eff}/Cu, μ_B	
	obsd	calcd	obsd	calcd
245.	3.382	3.473	1.82	1.84
204.	4.039	4.042	1.82	1.81
183.	4.510	4.400	1.82	1.80
143.	5.274	5.322	1.73	1.74
123.	5.773	5.914	1.68	1.70
103.	6.438	6.590	1.63	1.64
94.2	6.822	6.908	1.60	1.61
86.1	6.982	7.211	1.55	1.58
76.9	7.270	7.538	1.50	1.52
67.0	7.502	7.817	1.42	1.45
61.6	7.517	7.901	1.36	1.40
55.9	7.484	7.899	1.29	1.33
50.2	7.395	7.753	1.21	1.25
44.8	6.944	7.418	1.12	1.15
41.8	6.667	7.126	1.06	1.00
38.8	6.358	6.741	0.993	1.02
35.3	5.917	6.161	0.914	0.933
31.9	5.409	5.444	0.831	0.833
28.6	4.655	4.636	0.745	0.728
24.9	4.096	3.648	0.639	0.603
22.8	3.757	3.076	0.585	0.529

Table IV (continued)

21.6	3.575	2.785	0.556	0.491
20.5	3.316	2.512	0.525	0.454
17.8	2.915	1.986	0.456	0.376
15.0	2.469	1.676	0.386	0.318
13.2	2.391	1.631	0.355	0.293
11.1	2.384	1.753	0.326	0.279
10.7	2.363	1.803	0.318	0.278
10.2	2.394	1.860	0.313	0.276
9.81	2.362	1.928	0.304	0.275
9.38	2.376	2.004	0.299	0.274
8.94	2.341	2.091	0.289	0.273
8.54	2.335	2.180	0.282	0.273
8.15	2.351	2.276	0.277	0.272
7.75	2.252	2.386	0.264	0.272
7.36	2.292	2.505	0.260	0.272
6.96	2.222	2.642	0.249	0.271
6.37	2.335	2.875	0.244	0.271
4.84	2.145	3.745	0.204	0.269

Table V. Magnetic Exchange Parameters

Complex	J, cm^{-1}
Mn(II)Mn(II)LBF_4	-2.8
Fe(II)Fe(II)LBF_4	-0.8
Co(II)Co(II)$LBF_4 \cdot H_2O$	-0.9
Cu(II)Cu(II)$LBF_4 \cdot H_2O$	-33.5

Figure Captions

Figure 1. Molar paramagnetic susceptibility, χ_M, and effective magnetic moment, μ_{eff}/Mn, vs. temperature and least-squares fit of the data for Mn(II)Mn(II)LBF$_4$.

Figure 2. Molar paramagnetic susceptibility, χ_M, and effective magnetic moment, μ_{eff}/Fe, vs. temperature and least-squares fit of the data for Fe(II)Fe(II)LBF$_4$.

Figure 3. Molar paramagnetic susceptibility, χ_M, and effective magnetic moment, μ_{eff}/Co, vs. temperature and least-squares fit of the data for Co(II)Co(II)LBF$_4$ · H$_2$O.

Figure 4. Molar paramagnetic susceptibility, χ_M, and effective magnetic moment, μ_{eff}/Cu, vs. temperature and least-squares fit of the data for Cu(II)Cu(II)LBF$_4$ · H$_2$O.

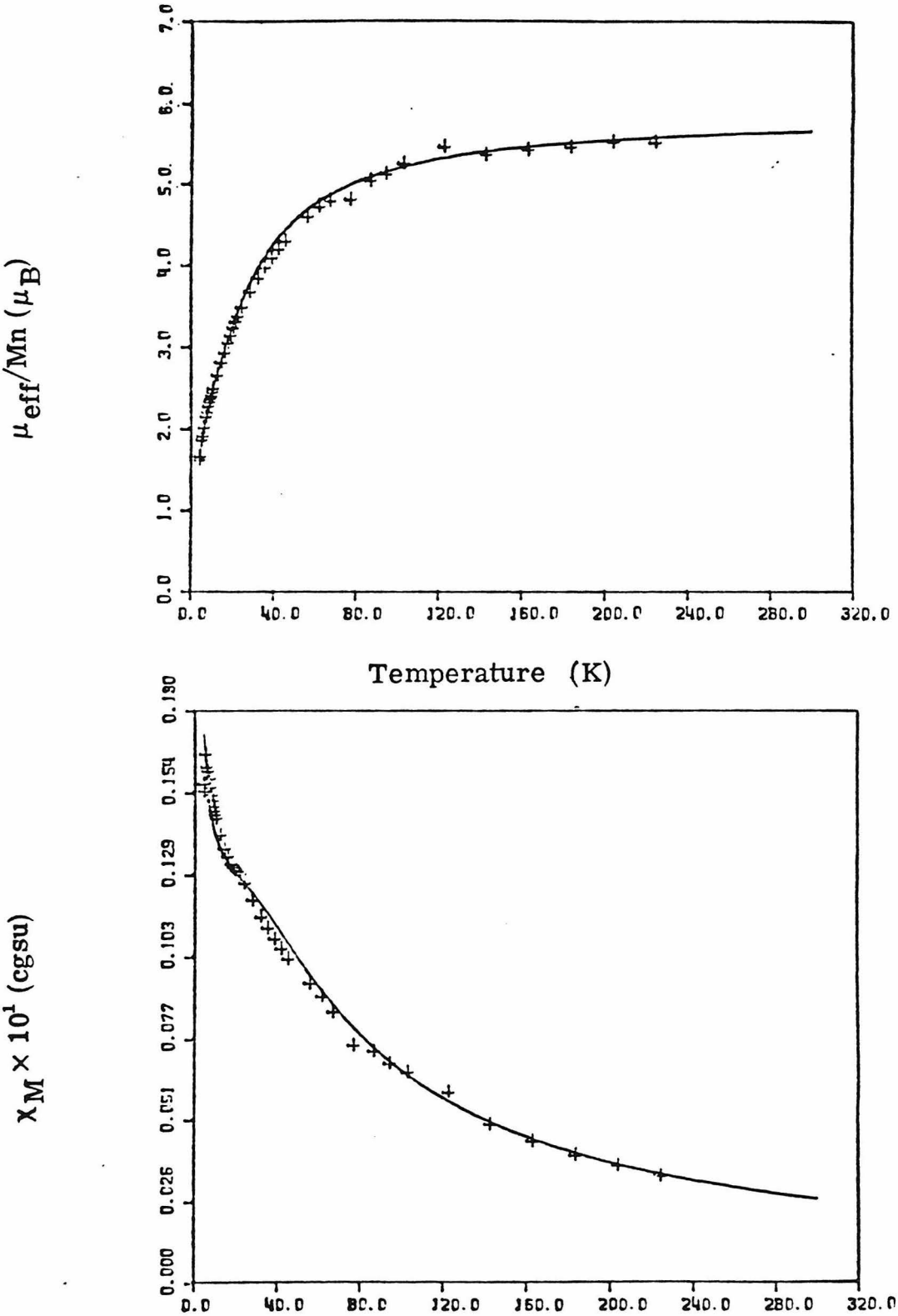
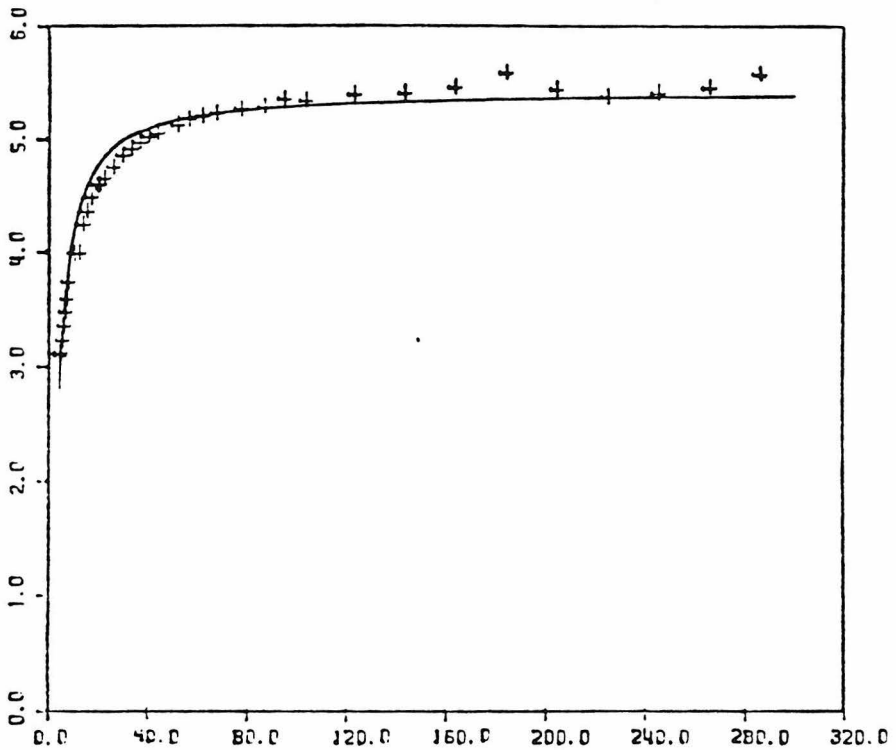
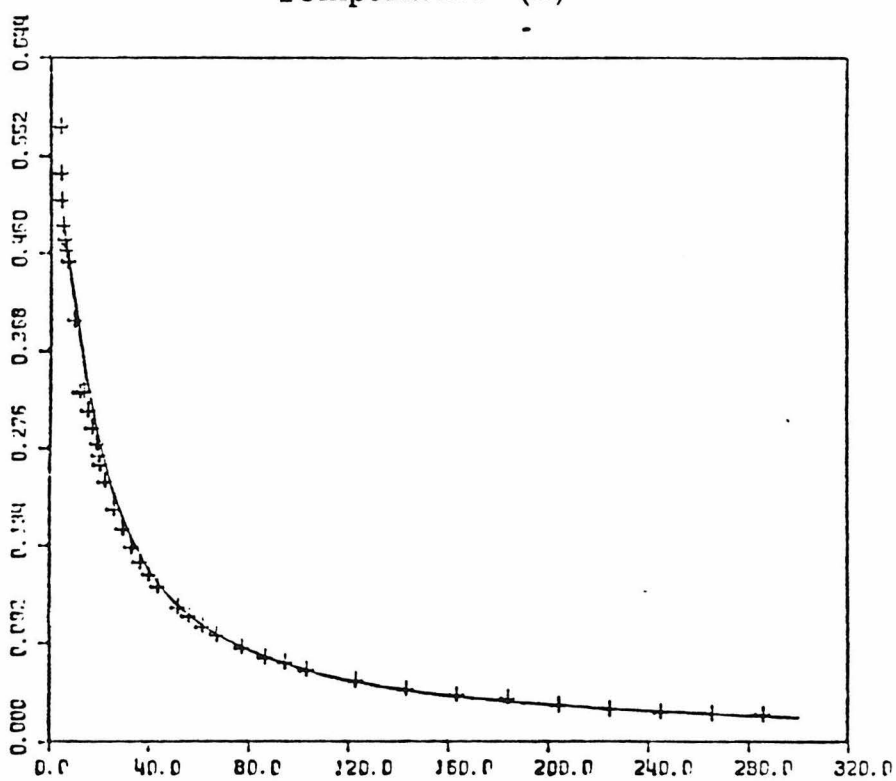

μ_{eff}/Mn (μ_B)
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
0.0
40.0
80.0
120.0
160.0
200.0
240.0
280.0
320.0
Temperature (K)
$\chi_M \times 10^1$ (cgsu)
0.000
0.026
0.051
0.077
0.103
0.129
0.154
0.180
0.0
40.0
80.0
120.0
160.0
200.0
240.0
280.0
320.0
Temperature (K)

Figure 1.

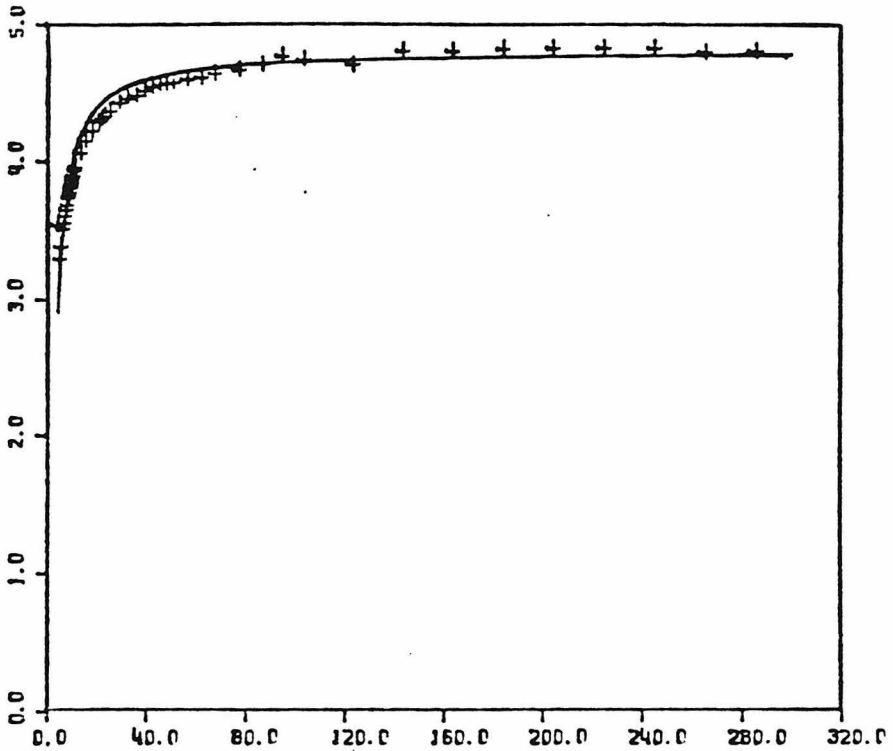


μ_{eff}/Fe (μ_B)

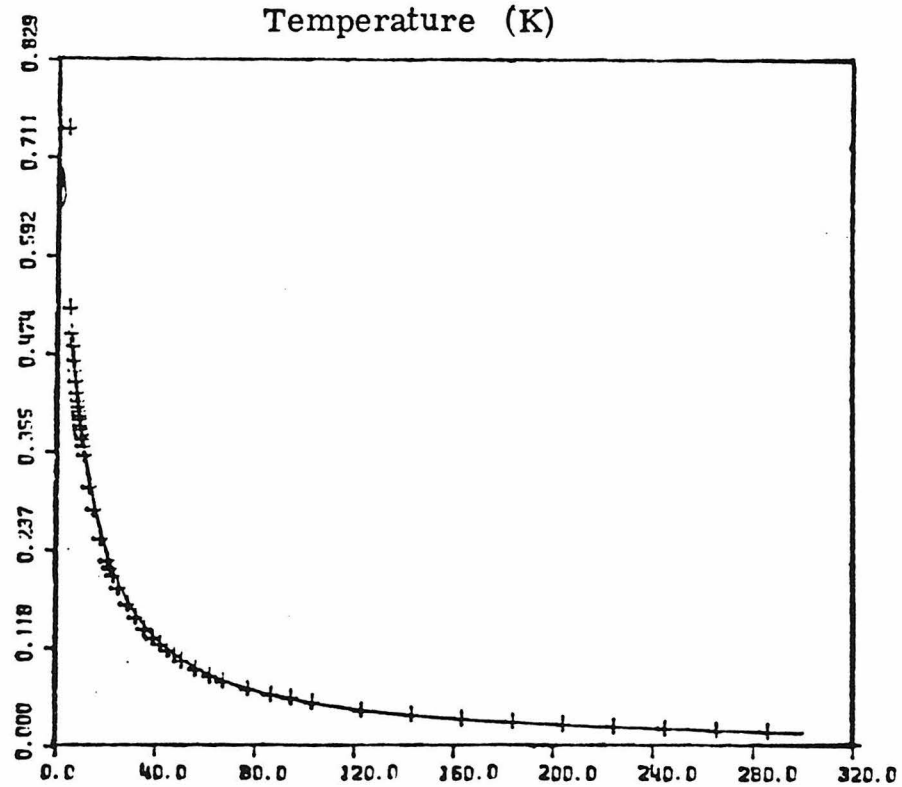


$\chi_M \times 10^1$ (cgsu)

Figure 2.

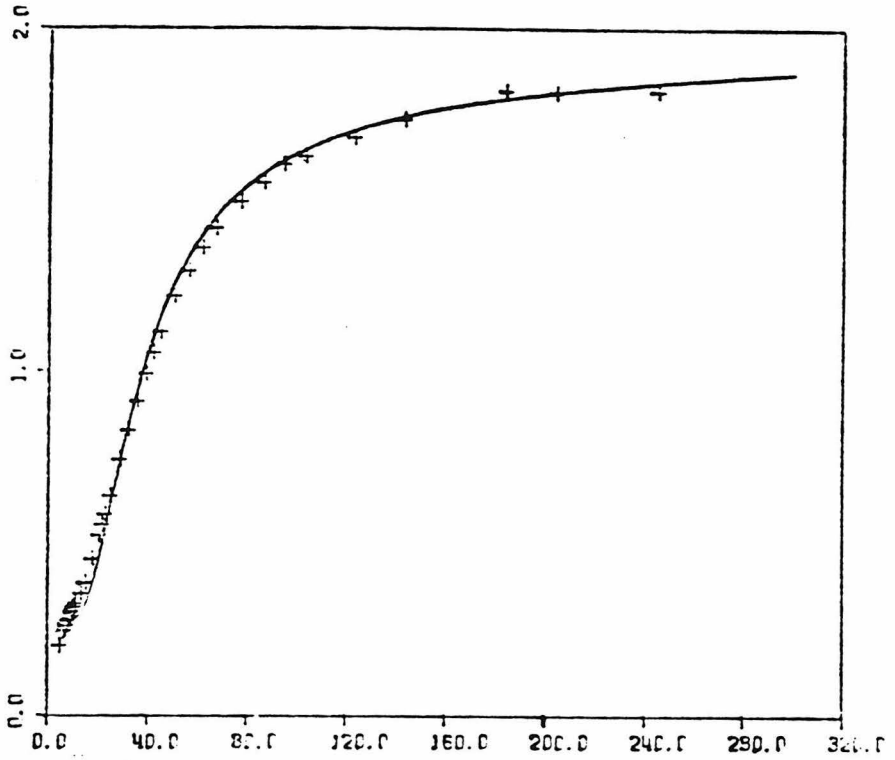


μ_{eff}/Co (μ_B)



$\chi_M \times 10^1$ (cgsu)

Figure 3.


2.0
1.0
0.0
0.0
40.0
80.0
120.0
160.0
200.0
240.0
280.0
320.0
μ_{eff}/Cu (μ_B)
Temperature (K)

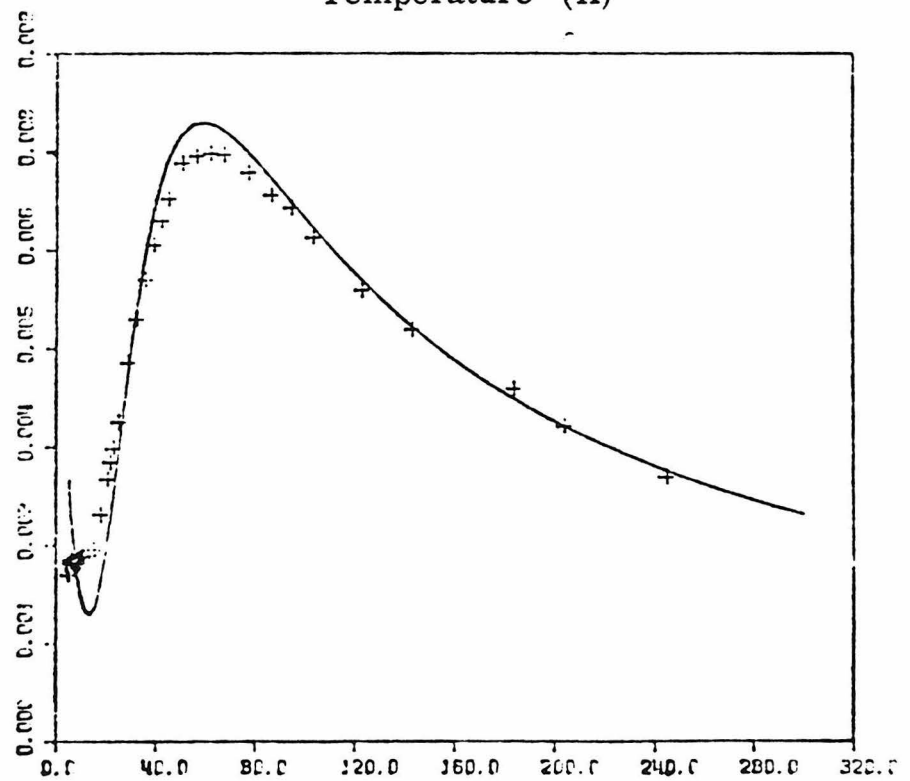

0.000
0.001
0.002
0.003
0.004
0.005
0.006
0.007
0.008
0.009
0.0
40.0
80.0
120.0
160.0
200.0
240.0
280.0
320.0
$\chi_M \times 10^3$ (cgsu)
Temperature (K)

Figure 4.

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APPENDIX I

Mononuclear and Binuclear Metal Complexes of 1,3-Bis(2-pyridylimino)isoindolines

Robert R. Gagné, William A. Marritt,
David N. Marks, and Walter O. Siegl

Mononuclear and Binuclear Metal Complexes of 1,3-Bis(2-pyridylimino)isoindolines

Robert R. Gagné,[1a] William A. Marritt,[1a]
David N. Marks,[1a] and Walter O. Siegl[1b]

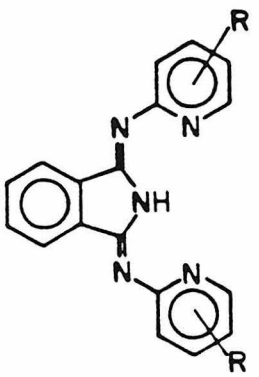
Contribution No. 6297 from the Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, and the Ford Motor Company, Engineering and Research Staff, Dearborn, Michigan 48121

Abstract

Condensation of 1,2-dicyanobenzene and 2-amino-4-methylpyridine resulted in the formation of 4'-MeLH, which in its anionic form functions as a tridentate chelating ligand. Metal complexes were prepared with metal to ligand ratios of 1:1 and 1:2. The 1:1 complexes also contain acetate as a ligand while in the 1:2 complex the two tridentate ligands provide a pseudooctahedral environment about the metal ion. An analogous binucleating ligand was prepared by reaction of 1,2,4,5-tetracyanobenzene and 2-amino-4-sec-butylpyridine. This ligand, as a dianion, is capable of binding two metal ions, providing three coordination sites for each. Complexes were prepared in which the remaining coordination sites are either occupied by 4'-MeLH, resulting in two six-coordinate metal ions, or by an acetate ligand. Mononuclear and binuclear complexes were prepared with Mn(II), Fe(II), Co(II), Co(III), Ni(II), Cu(II), and Zn(II). Magnetic, spectral and electrochemical properties of these molecules were investigated.

INTRODUCTION

Stable metal complexes of the ligand 1 have been prepared with ligand to metal ratios of 2:1 and 1:1.[2] The ligand functions as an

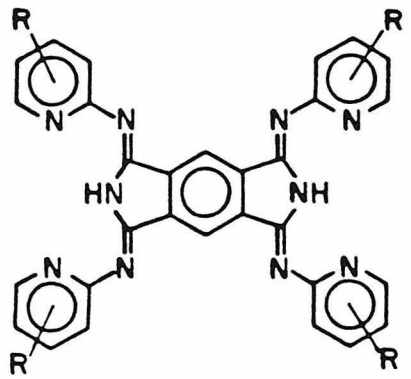


1

LH,[3] R = H

4'-MeLH, R = 4'-CH_3

anionic tridentate chelate capable of occupying three coplanar sites about the metal ion and forming a pseudooctahedral environment around the metal ion in the bis-(ligand) complex, ML_2.[3] Metal complexes with M = Fe(II), Co(II), NI(II), Zn(II) and Cd(II) have been reported, but little had been done to characterize these molecules. These complexes became of greater interest after the synthesis of the conjugated organic molecule 2, which may function as a bridging ligand between two metal ions.[4] This molecule made it possible to prepare not only binuclear metal complexes but also polymeric metal species. The polymeric complexes were of great interest for two reasons: polynuclear complexes offer a chance to study metal-metal interactions via electrochemistry and magnetic measurements, and complexes of this type are



HL-LH,[3] R = 4′-sec-butyl

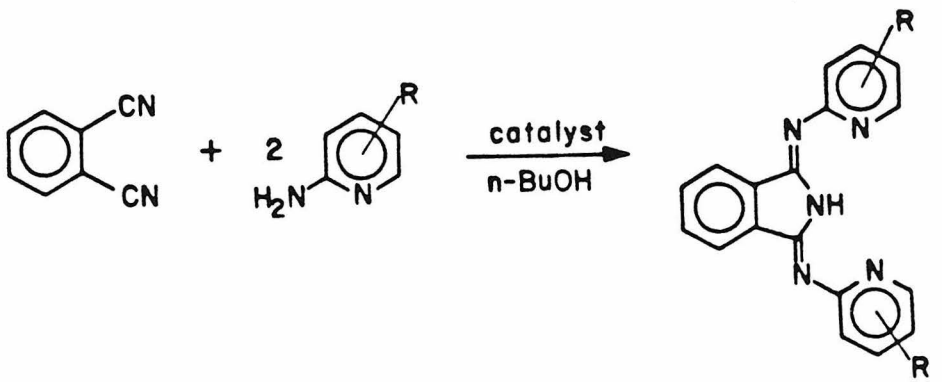
2

interesting candidates for reactions involving multielectron transfer. We report here the preparation and certain physical properties of mononuclear and binuclear metal complexes with Mn(II), Fe(II), Co(II), Co(III), Ni(II), Cu(II) and Zn(II).

RESULTS AND DISCUSSION

Synthesis and Characterization of the Ligands. Two general syntheses of mononucleating, 1,3-bis(arylimino)isoindoline ligands RLH (1) involving metal ion-assisted condensation of phthalonitrile with a 2-aminopyridine or other 2-amino heterocycles were described earlier[5] (eq 1).

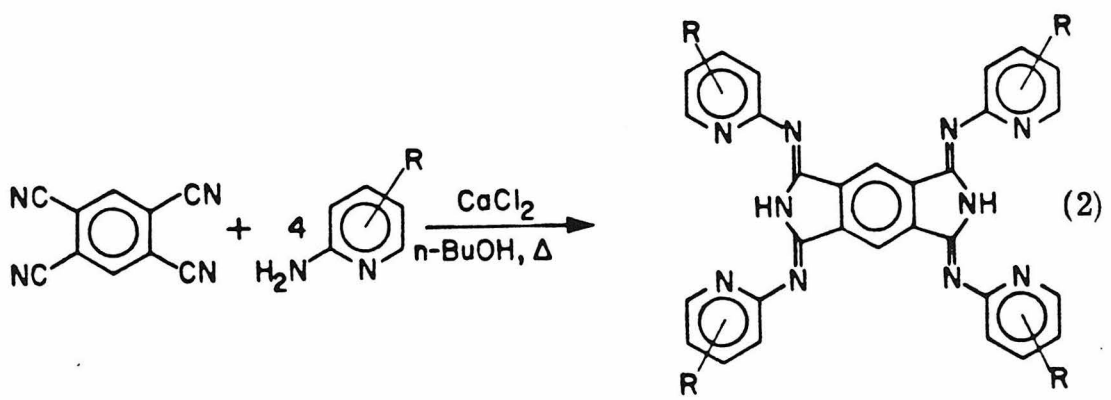
The binucleating ligand 2 was prepared in a similar manner by these methods as shown in eq 2 and 3. The method of choice afforded the binucleating ligand in good yield from a one-flask synthesis utilizing an alkaline-earth salt (anhydrous $CaCl_2$) to catalyze the condensation of tetracyanobenzene with 4 equiv of aromatic amine. A second method,



(1)

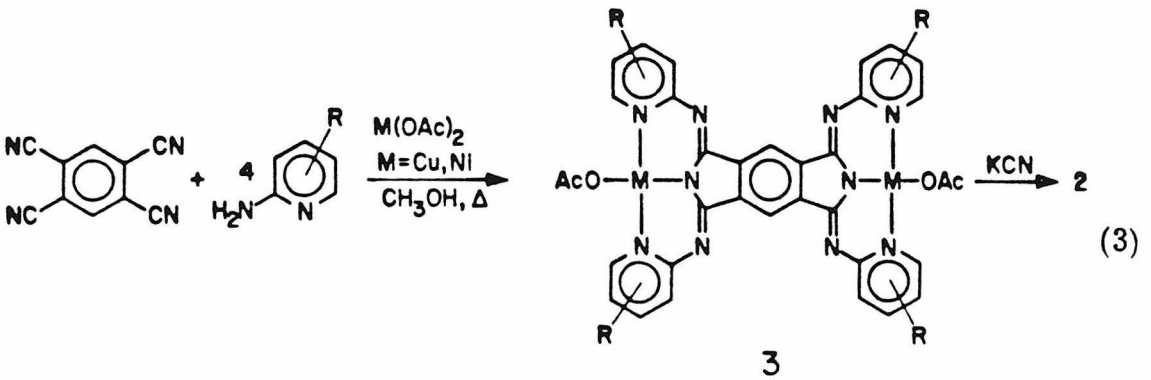
1

a template-type synthesis, utilized Ni(II) or Cu(II) acetate to facilitate the condensation, affording initially the metal complex 3, which was subsequently treated with KCN to produce free binucleating ligand, 2. Attempts to prepare ligand 2 via alkoxide catalysis resulted in the production of significant amounts of blue-purple pigment, possibly phthalocyanine impurities.



(2)

2



(3)

3

A series of binucleating ligands was prepared from tetracyanobenzene and various alkyl-substituted 2-aminopyridines for the purpose of obtaining a ligand with acceptable solubility in organic solvents. The bridging ligands are all high melting, yellow crystalline solids and with the exception of the 4′-n-propyl and 4′-tert-butyl derivatives, which are somewhat hygroscopic, have long shelf lives. Solubilities vary over a range of two orders of magnitude as shown in Table I, with the 4′-sec-butyl derivative being the most soluble; unless indicated otherwise, all work described in this paper was carried out with the 4′-sec-butyl substituted ligand, HL-LH.

The rather complex infrared spectra of the bridging ligands contain characteristic bands in the 1650-1500 cm^{-1} region, ca. 1640 (m-s) and 1590 (s) (also a band at ca. 1540 (m) observed for the 4′-alkyl-substituted ligands), which undergo changes upon chelation of a metal ion. The infrared spectrum of the chelated ligand exhibits only a much weaker band at 1640 cm^{-1} and a shift of the 1590 cm^{-1} band to lower energy; two new bands appear at ca. 1610 and 1525-1515 cm^{-1}. These

Table I. Yields, Melting Points, and Relative Solubilities for the Binucleating Ligands, 2.

Cpd.	Derived from (amine)	Yield	Melting Point (°C)	Relative Solubility
2a	2-aminopyridine	90	324-6	2.6
2b	2-amino-4-methylpyridine[a]	59	340-1	1
2c	2-amino-5-methylpyridine	79	345-8 (dec)	ND
2d	2-amino-3,5-dimethylpyridine	ND[b]	375-7	ND
2e	2-amino-4-ethylpyridine	45	353-5	72
2f	2-amino-4-n-propylpyridine[a]	58	357-9	52
2g	2-amino-4-sec-butylpyridine	83	369-71	105
2h	2-amino-tert-butylpyridine[a]	44	435-7	1.7
2i	2-amino-4-n-amylpyridine	49	317-18	11

[a]Ligand isolated as a monohydrate.

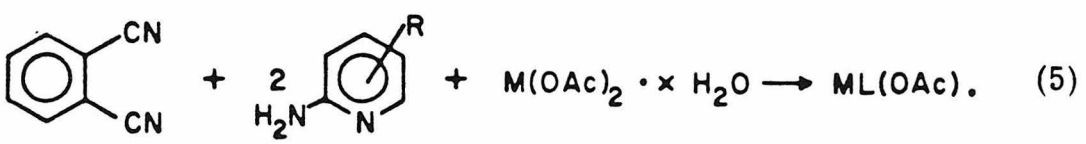
[b]ND = not determined.

generalizations appear to be true for a variety of substituted ligands and metal ions.

Proton NMR spectra were obtained only for the most soluble of the 4'-alkyl-substituted ligands. The benzo protons appear as a singlet at 8.60-8.70 ppm ($CDCl_3$) and the pyridyl protons are shifted in the general order of $H_5 < H_3 < H_6$ as reported earlier for the mononucleating ligands $\underset{\sim}{1}$.[5]

Synthesis and Characterization of Mononuclear Metal Complexes. Mononuclear divalent metal complexes of the type $ML(OAc)^3$ (M = Mn, Fe, Co, Ni, Cu, and Zn) are readily formed upon treatment of the free ligand with excess metal acetate in alcohol (eq 4). The reaction is rapid at ambient temperature, affording highly colored crystalline solids. All were air and thermally stable in the solid state, although Mn(II), Fe(II), and Co(II) complexes were, to some extent, air sensitive in solution; the latter were prepared under an inert atmosphere. The Co(II), Ni(II), Cu(II), and Zn(II) complexes were also prepared by a template reaction directly from phthalonitrile, amine, and metal salts (eq 5).[6]

$$\underset{\sim}{1} + M(OAc)_2 \cdot xH_2O \longrightarrow ML(OAc) \qquad (4)$$



(5)

With the exception of the Zn(II) complex, all of the complexes, ML(OAc), were paramagnetic. The infrared spectra are dominated by ligand bands; changes observed in the spectrum of the mono-nucleating ligand upon coordination to a metal ion are analogous to those described above for the bridging ligand.

Treatment of a divalent transition metal salt (Mn, Fe, Co, Ni, Cu, Zn) with 2 equiv of chelating ligand afforded the neutral complex ML_2 in high yields, as indicated in eq 6.

$$MX_2 + 2LH \rightarrow ML_2 + 2HX. \quad (6)$$

For metal salts with very poor bases as counterions, e.g., ClO_4^-, an amine base was usually added to facilitate deprotonation of the ligand; however, with Cl^- or OAc^-, no external base was required.

Alternatively, the ML_2-type complexes could be prepared in a two-step process by subsequently treating the product of eq 4 with a second equivalent of chelating ligand, as shown in eq 7. The two-step

$$ML(OAc) + LH \rightarrow ML_2 \quad (7)$$

approach allows the preparation of complexes with two different ligands, as indicated in eq 8.

$$ML(OAc) + L'H \rightarrow MLL'. \quad (8)$$

The synthesis of such unsymmetrically substituted (chelated) complexes was usually carried out under conditions whereby the product precipitated from solution, thus minimizing the possiblity of ligand scrambling. Evidence that asymmetric synthesis (eq 8) could be carried out for

Co(II) without ligand scrambling was obtained from cyclic voltammetric measurements on the mixed ligand complex Co(4′-MeL)(5′-ClL). The complex Co(4′-MeL)(5′-ClL) exhibited a single wave at 0.081 V vs. NHE, whereas a mixture would have given two waves at -0.094 V vs. NHE for $Co(4'\text{-MeL})_2$ and at 0.235 V vs. NHE for $Co(5'\text{-ClL})_2$.

The observation that ligand exchange could occur in solution, even at room temperature, was made from a series of metal-exchange experiments. Cupric ion readily replaces substitution-labile metal ions such as Co(II), Ni(II), and Zn(II) from complexes of types ML(OAc) and ML_2. However, no exchange occurs with cupric ion and substitution inert Co(III) in $Co(4'\text{-MeL})_2PF_6$.

The ML_2 complexes of metal ions with unfilled d shells are all dark, intensely colored crystalline solids. In general, the ML_2 complexes have much greater solubilities in organic solvents than the corresponding ML(OAc) complexes; typically, they are soluble in solvents of low polarity such as cyclohexane or toluene, but only sparingly soluble in very polar solvents such as methanol.[7] Infrared spectra are essentially identical to spectra of the corresponding ML(OAc) complexes. The NMR spectra, magnetic properties, and electrochemistry are discussed in a later section.

The Co(II) complex, $Co(4'\text{-MeL})_2$, was oxidized with ceric ion to the corresponding Co(III) complex, diamagnetic $Co(4'\text{-MeL})_2^+$, and isolated as its BF_4^-, BPh_4^-, and PF_6^- salts. Attempts to similarly prepare $Mn(4'\text{-MeL})_2^+$ were unsuccessful. Complexes of Fe(III) could be prepared by ferricenium oxidation of $Fe(4'\text{-MeL})_2$; however, they

were unstable in polar solvents, apparently dissociating one of the tridentate ligands.

Synthesis and Characterization of Binuclear Complexes. The preparation of homonuclear complexes with the binucleating ligand HL-LH, 2, parallels the preparation of mononuclear complexes with the mononucleating ligand 1. The simplest binuclear complexes were obtained by treatment of the bridging ligand with an excess of metal acetate, as shown in eq 9 [M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II)].[3] The same binuclear complexes of Ni(II) and Cu(II) were

$$\text{HL-LH} + \text{excess } M(OAc)_2 \rightarrow (AcO)ML\text{-}LM(OAc) \qquad (9)$$

obtained via the template route shown in eq 3, although the purity of complexes obtained via the template route was lower. The relatively low solubility of the (AcO)ML-LM(OAc) complexes made purification using solution techniques impractical, and accordingly eq 9 was the preferred route. The new complexes are intensely colored and have high thermal stability. The characteristic changes observed in the infrared spectrum upon coordination of ligand 2 with metal ions was discussed earlier.

The binuclear complexes, (OAc)ML-LM(OAc) (3), react readily with mononucleating ligand, LH (1), as shown in eq 10, a procedure analogous to the formation of MLL′ described by eq 8. The preparation

$$\underset{3}{(AcO)ML\text{-}LM(OAc)} + 2LH \rightarrow \underset{4}{LML\text{-}LML} \qquad (10)$$

$$HL\text{-}LH + 2ML(OAc) \rightarrow LML\text{-}LML \qquad (11)$$

$$\underset{\sim}{4}$$

of this new series of binuclear complexes, $\underset{\sim}{4}$, can also be approached by treating the bridging ligand with 2 equiv of ML(OAc) according to eq 11.

The two metal ions in the complexes LML-LML ($\underset{\sim}{4}$) are encapsulated by organic ligands similar to ML_2 and accordingly have significantly increased solubility in organic solvents when compared with the binuclear complexes $\underset{\sim}{3}$, allowing the application of solution techniques for characterization. The monomeric nature of these complexes is suggested by a molecular weight determination (in toluene) on ((4′-sec-butyl)L)NiL-LNi((4′-sec-butyl)L) which yielded a value of 1699 compared with a calculated value of 1680.

Attempts to prepare (4′-MeL)FeL-LFe(4′-MeL) by the approaches outlined above (eq 10 and 11) were unsuccessful. The mononuclear metal complex, Fe(4′-MeLH)Br_2 (coordinated 4′-MeLH is protonated presumably at one of the imine nitrogens), obtained from the reaction of 4′-MeLH with excess ferrous bromide in alcohol, proved a useful starting material for preparing (4′-MeL)FeL-LFe(4′-MeL). Treatment of deprotonated binucleating ligand with an excess of Fe(4′-MeLH)Br_2 yielded the desired binuclear Fe(II) complex.

The infrared spectra of binuclear M(II) complexes are very similar to those of ML_2. Proton NMR spectra and magnetic and electrochemical properties are discussed below.

The cobalt complex (4′-MeL)CoL-LCo(4′-MeL) was successfully

oxidized with ceric ion to the corresponding Co(III) complex and isolated as its BPh_4^- and PF_6^- salts.

Magnetic Susceptibility. Table II gives values of μ_{eff} for both mononuclear and binuclear M(II) complexes, all of which are high spin. Magnetic measurements have been made on (AcO)CuL-LCu(OAc) over a range of temperatures from liquid helium to room temperature. The results of these measurements show a very slight metal-metal interaction with $J = -1\ cm^{-1}$.[8] In general, the magnetic moments of binuclear complexes are slightly lower per metal ion than the moments of the corresponding mononuclear complexes. It is unlikely that these lower values result from magnetic coupling but are probably attributable to trace impurities.

Electronic Absorption Spectra. The visible spectra of all mononuclear and binuclear complexes show intense ($\epsilon \sim 20\text{-}50,000$) ligand absorptions in the range 400-450 nm. All of the complexes are yellow in dilute solution as is the ligand. For the metal complexes, the high energy ligand absorptions are fairly broad so that concentrated solutions (~ 10 mM) are nearly black, and ligand field absorptions could not be identified.

The mononuclear iron (II) complex shows two broad absorptions at 650 nm and 740 nm ($\epsilon \sim 800$) in addition to the ligand absorptions. These bands may be assigned, due to their position and intensity, as Fe(II) $\rightarrow$ L charge transfer bands.

Proton NMR Spectra. Proton NMR spectra were obtained for the mononuclear Fe(II), Co(II), Co(III), Ni(II), and Zn(II) complexes,

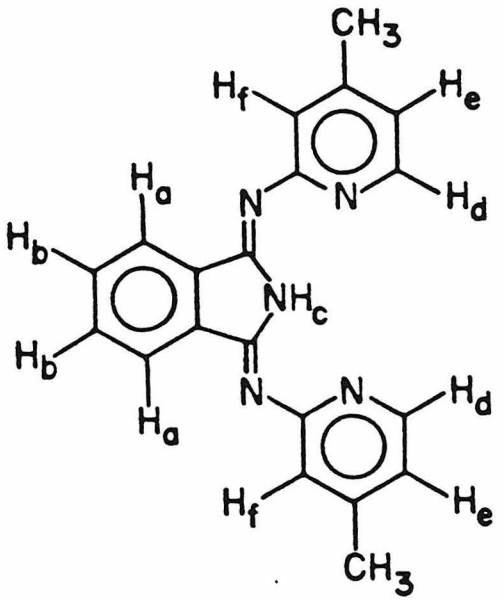
$M(4'\text{-MeL})_2$, to identify the complexes and to test their purity (Table III). Spectra of the Mn(II) and Cu(II) complexes are severely broadened due to the slow electron-relaxation times of these metals. In the diamagnetic complexes, the protons could be assigned with no ambiguity from the splitting pattern of the peaks. In contrast, peak widths for the paramagnetic complexes of approximately 0.2 ppm totally overwhelmed any splitting. For this reason assignment was more difficult and less reliable. In general, NMR spectra of all the paramagnetic complexes are very similar. The protons in the paramagnetic species were assigned by using integration data and by trends observed in the diamagnetic complexes and in other similar paramagnetic complexes.[9] The magnitude of the shift in the paramagnetic molecules was found to be dependent on the metal involved. Among the paramagnetic complexes, the protons α to the nitrogen of the pyridine ring, H_d, were observed only for the Co(II) complex and appear far downfield at 106 ppm. This resonance is extremely broad due to the nearness of these protons to the paramagnetic center. Similar behavior was reported for $Co(phen)_3^{2+}$.[10]

The binuclear products gave very complex spectra. The diamagnetic Co(III) complex, however, gave a particularly well resolved spectrum (Figure 1), permitting analysis. Integrations of sec-butyl protons and methyl protons gave the expected ratio for one binucleating ligand and two mononucleating ligands per complex, helping to substantiate that this complex is binuclear and not a higher order polymer. The aromatic protons were difficult to assign due to overlapping peaks in this region of the spectrum.

Table II. Magnetic Susceptibility Data for Mononuclear and Binuclear Complexes per Metal Ion.

Complex	μ_{eff} (B.M. 298 K)
$Mn(4'\text{-MeL})_2$	5.92
$Fe(4'\text{-MeL})_2$	5.12
$Co(4'\text{-MeL})_2$	4.85
$Ni(4'\text{-MeL})_2$	3.10
$Cu(4'\text{-}\underline{sec}\text{-butylL})_2$	1.85
(4'-MeL)MnL-LMn(4'-MeL)	5.66
(4'-MeL)FeL-LFe(4'-MeL)	5.13
(4'-MeL)CoL-LCo(4'-MeL)	4.65
(4'-MeL)NiL-LNi(4'-MeL)	3.07
(4'-MeL)CuL-LCu(4'-MeL)	1.83

Table III. Proton NMR Data for Mononuclear Complexes in $CDCl_3$. Values are given as δ, ppm, vs. TMS at 34°C.



Proton	4′-MeLH	Zn(II)	Co(III)	Co(II)	Ni(II)	Fe(II)
H_a	8.01	8.04	8.13	26.5	13.0	11.0
H_b	7.54	7.55	7.76	26.0	11.9	9.0
H_c	13.97					
H_d	8.40	7.93	7.37	106	--	--
H_e	6.83	6.35	6.62	35.6	33.1	31.6
H_f	7.23	7.07	7.10	43.7	51.1	41.5
CH_3	2.30	2.07	2.31	-15.7	-6.3	-24.8

Figure 1. Proton NMR spectrum of (4'-MeL)CoL-LCo(4'-MeL)$(ClO_4)_2$ in $CDCl_3$ at 34°C. Integration of the sec-butyl protons (0.8 and 1.1 ppm) and the methyl protons (2.3 ppm) provide evidence for describing the complex as binuclear.

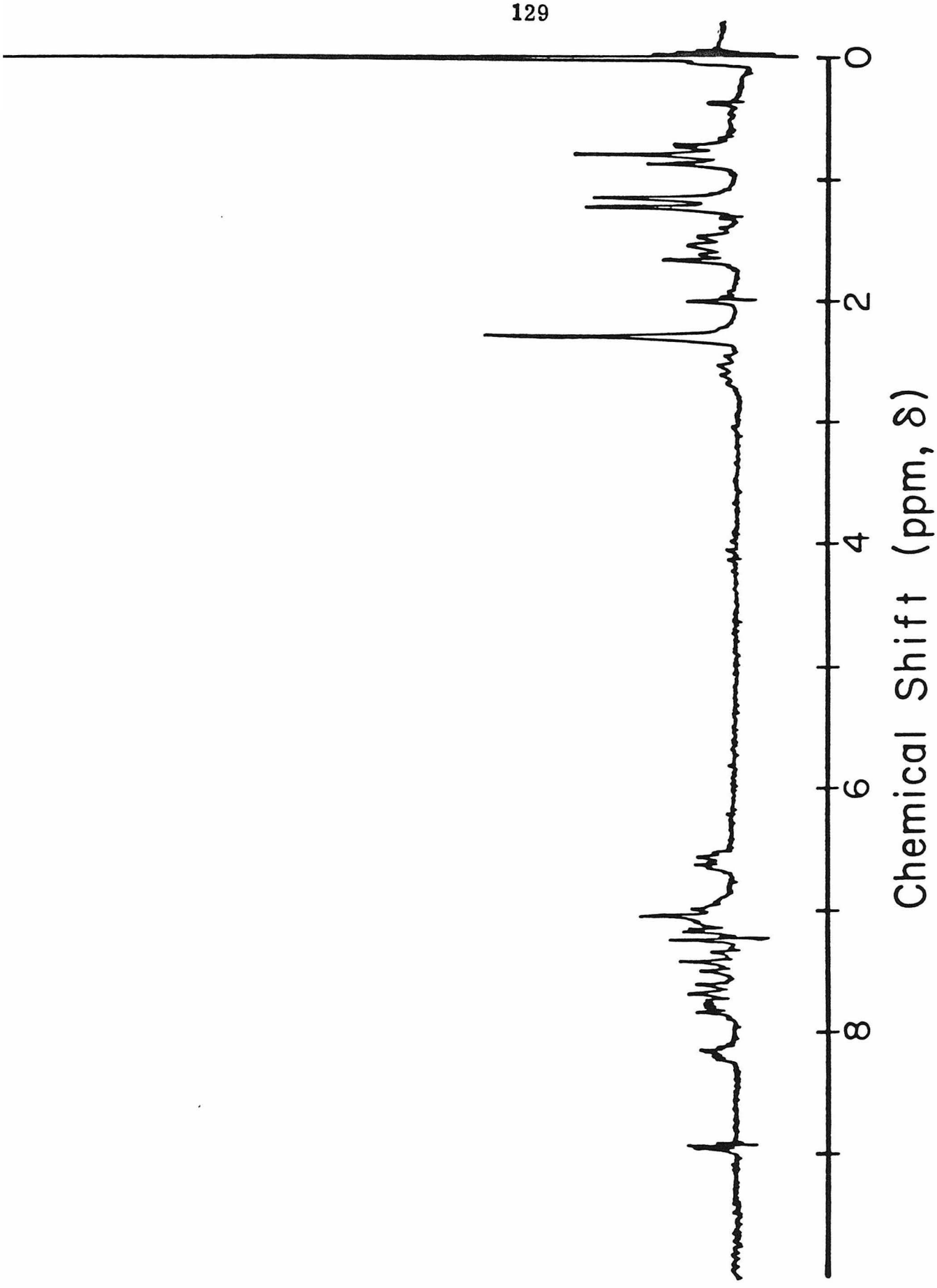

0
2
4
6
8
Chemical Shift (ppm, δ)

Table IV. Electrochemical Potentials for Mononuclear and Binuclear Complexes as Measured in DMF (vs. NHE).

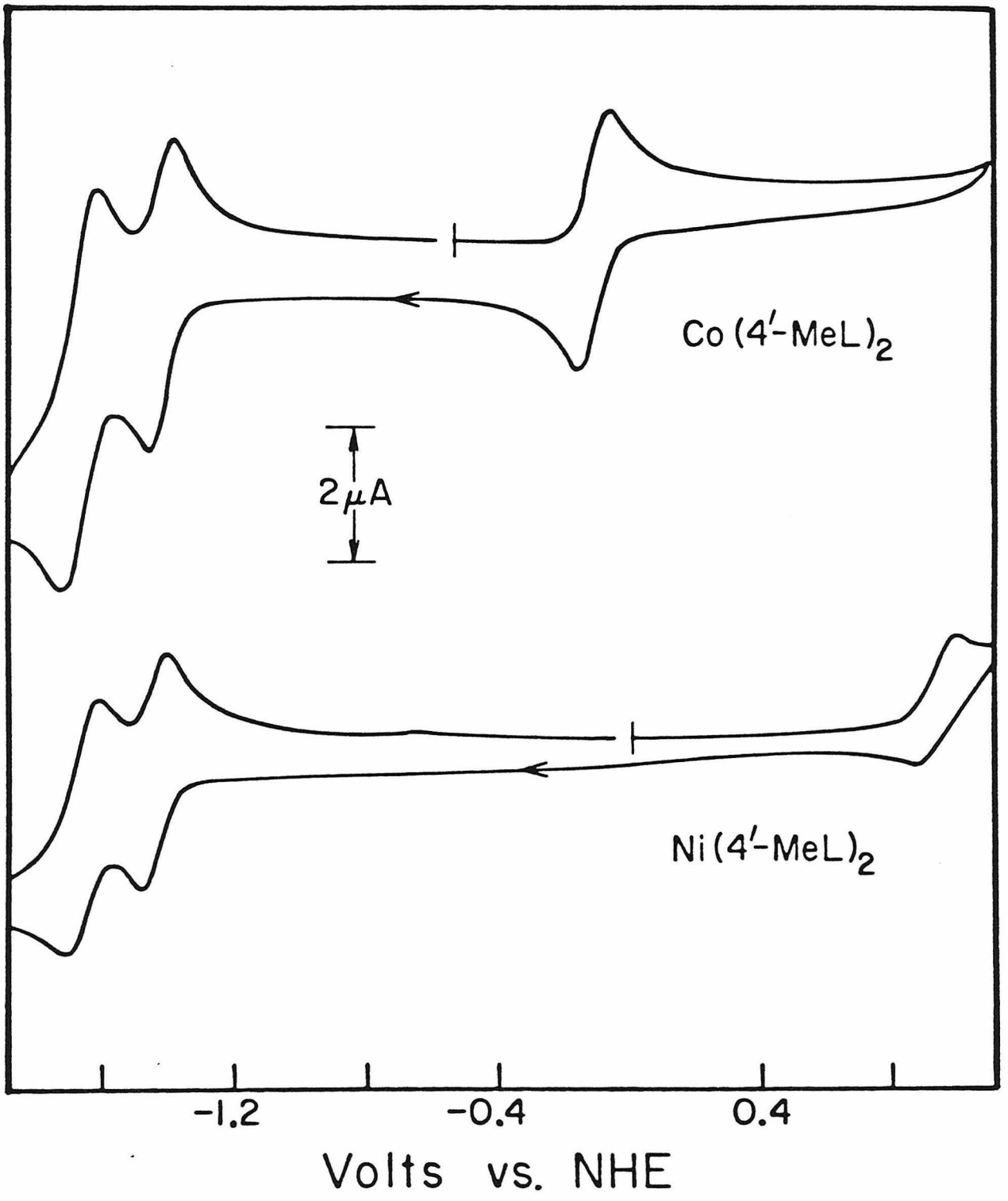
Complex	M(II/III)		n[b]	Ligand waves, E^f			
	E^f	$E_{p_a} - E_{p_c}$ [a]					
$Mn(4'\text{-MeL})_2$	0.310	90	1.00		-1.438	-1.652	
$Fe(4'\text{-MeL})_2$	0.130	65	0.99		-1.460	-1.680	
$Co(4'\text{-MeL})_2$	-0.094	90	0.95		-1.420	-1.680	
$Ni(4'\text{-MeL})_2$	0.954	90	1.01		-1.435	-1.664	
$Zn(4'\text{-MeL})_2$	--	--	--		-1.470	-1.660	
(4'-MeL)MnL-LMn(4'-MeL)	0.323	240	2.04	-1.173	-1.418	-1.600	
(4'-MeL)FeL-LFe(4'-MeL)	0.182	100	2.04	-1.204	-1.494	-1.642	-1.758
(4'-MeL)CoL-LCo(4'-MeL)	-0.045	160	1.90	-1.185	-1.455	-1.640	
(4'-MeL)NiL-LNi(4'-MeL)	0.976[c]		2.10	-1.190	-1.477	-1.650	

[a] Anodic peak to cathodic peak separation of metal wave in cyclic voltammetry given in millivolts.

[b] Number of electrons involved in metal oxidation determined by constant potential electrolysis.

[c] Potentials were obtained by differential pulse voltammetry due to low solubility.

Figure 2. Cyclic voltammograms of DMF solutions: upper figure $Co(4'\text{-MeL})_2$; lower figure $Ni(4'\text{-MeL})_2$.


Co (4′-MeL)2
2μA
Ni (4′-MeL)2
-1.2
-0.4
0.4
Volts vs. NHE

The use of NMR spectroscopy to investigate intramolecular electron transfer in the mixed-valent $Co^{II}Co^{III}$ complex was attempted. Equilibrium concentrations of (4'-MeL)CoL-LCo(4'-MeL)$^{+}$ were generated by mixing equimolar amounts of (4'-MeL)CoL-LCo(4'-MeL) and (4'-MeL)CoL-LCo(4'-MeL)$^{2+}$. The mixture gave a spectrum that is very similar to the composite spectrum of (4'-MeL)CoL-LCo(4'-MeL) plus (4'-MeL)CoL-LCo(4'-MeL)$^{2+}$ but with several additional peaks. One of the peaks, which is very broad, sharpens into a single peak at -1.5 ppm at higher temperatures (~50°C) and resolves into two peaks at 4.3 ppm and -10.7 ppm as the temperature is lowered (~-50°C). This behavior is typical of a process whose rate is on the order of the NMR time scale. However, due to the complexity of these spectra and the chemical structures involved, it was not possible to assign this process to intramolecular electron transfer.

Electrochemistry. Electrochemical measurements have been made on all mononuclear and binuclear complexes (Table IV). Most complexes exhibited quasi-reversible behavior except for Cu(4'-sec-butyl L)$_2$ and all complexes having a single tridentate ligand, M(4'-MeL)OAc, for which both anodic and cathodic cyclic voltammetric waves could not be obtained. Cyclic voltammograms of mononuclear complexes, M(4'-MeL)$_2$ (e.g., Figure 2) consist of a metal oxidation wave and two reductions attributable to the ligand. The anodic and cathodic peak currents for the M(III)/M(II) couple are equal but the peak potential separation is larger than the expected 58 mV for a reversible one-electron process.[11] Coulometry at potentials anodic of

the metal oxidations verify that these are one-electron processes with $\underline{n} = 1.0 \pm 0.05$.

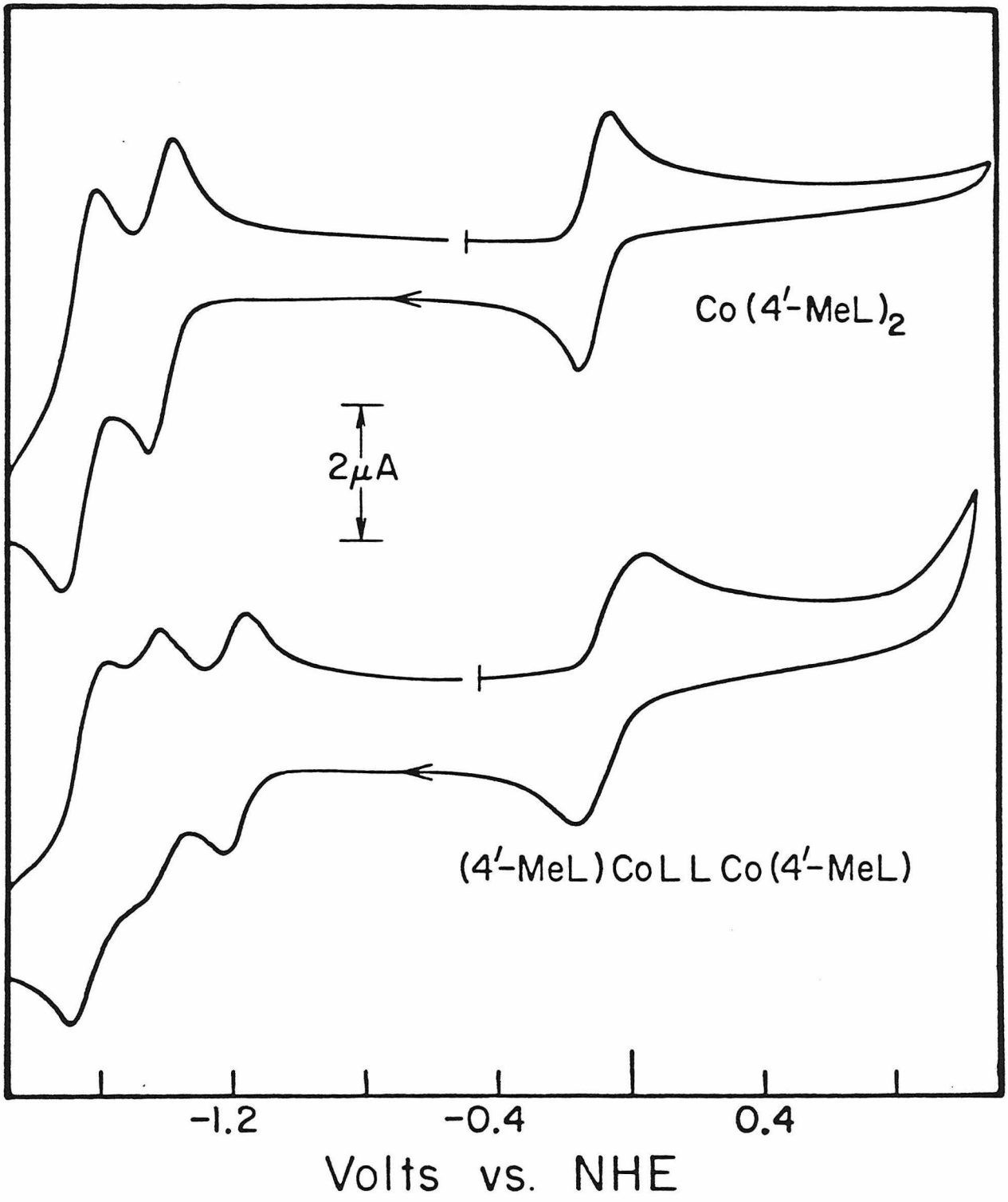
The metal reduction potentials of the binuclear complexes are very similar to potentials measured for the mononuclear complexes. The metal oxidation waves in the binuclear complexes are quite broad (Figure 3) and constant potential electrolyses anodic of these waves yields $\underline{n}$ values of 2.0 ± 0.1. This behavior is consistent with two closely spaced one-electron oxidations resulting in one broad wave. Similar behavior has been observed for some ruthenium dimers.[12] In general, the factors determining the potential difference between two consecutive redox processes in binuclear complexes are complex.[13] A separation of the two one-electron waves by 100 mV or less sets a range for the constant describing the comproportionation equilibrium (eq 12; $4 \leq K_{com} \leq 50$). The lower limit of 4 corresponds to com-

$$M(II)\,M(II) + M(III)\,M(III)^{2+} \rightleftharpoons 2M(II)\,M(III)^{+} \qquad (12)$$

pletely noninteracting metal centers, in which case one would expect a single electrochemical wave with $E_{p_a} - E_{p_c} = 58$ mV.[14]

The electrochemical results indicate that the binuclear complexes undergo a two-electron metal oxidation with the two electrons being transferred at nearly the same potential. One would then expect longer chain polymers to undergo multielectron oxidation with all of the electrons transferred at approximately the same potential. This may be a very desirable property for utilization of these complexes as multielectron-transfer catalysts.

Figure 3. Cyclic voltammograms of DMF solutions: upper figure $Co(4'\text{-MeL})_2$; lower figures (4'-MeL)CoL-LCo(4'-MeL).


Co (4′-MeL)2
2μA
(4′-MeL) Co L L Co (4′-MeL)
-1.2
-0.4
0.4
Volts vs. NHE

Cyclic voltammograms of the binuclear complexes also show three ligand reductions. Two of these reductions appear at approximately the same potential as reductions observed for the mononuclear complexes. The third ligand reduction appears at a more positive reduction potential and is presumably due to reduction of the bridging ligand. The binuclear Fe(II) complex shows a fourth reduction at even more negative potentials than the ligand reductions. The product of this reduction has not been investigated.

A series of mononuclear Co(II) complexes containing various substituents on the pyridine ring of the ligand were prepared in order to determine the effect of these substituents on the metal reduction potential (Table V). The results of these measurements show that the effect of the substituents is significant. A shift of nearly 700 mV is observed in going from a 4'-methyl to a 5'-nitro substituent. A plot of the reduction potential vs. the Hammett parameter of the substituent is approximately linear (Figure 4), as has been observed in certain other ligand systems.[15]

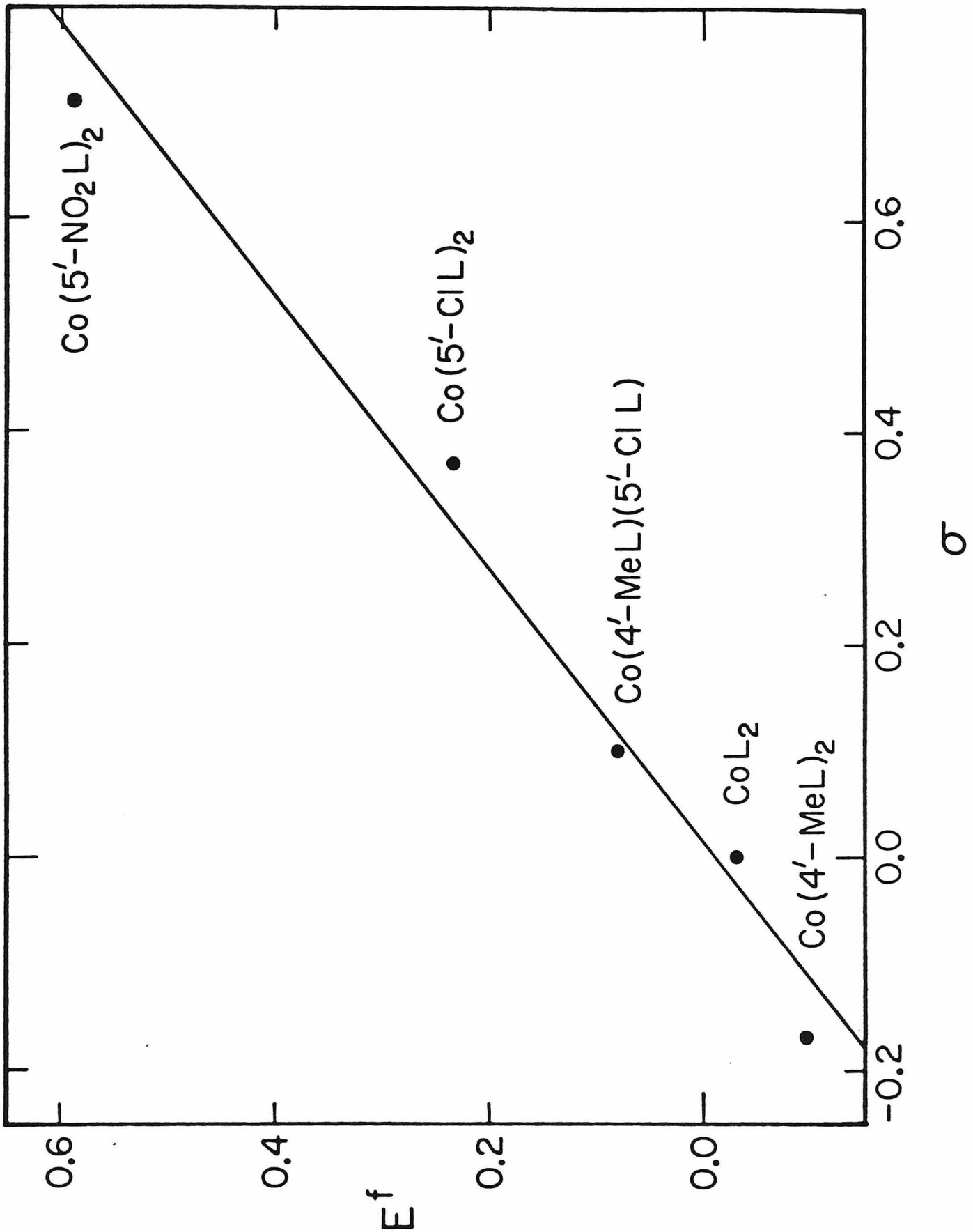
Thus, by changing the substituents, a large shift in reduction potential can be produced, making it possible to design a complex having specific redox chemistry. Accordingly, the reactivity of these complexes with various substrates might be significantly altered by the effects of these substituents on the reduction potential.

Table V. Cobalt (III)/Cobalt (II) Reduction Potentials, E^f, for Several $Co(RL)_2$.[a]

Complex	Co(III)/Co(II)
$Co(4'\text{-}MeL)_2$	-0.094 V
CoL_2	-0.031 V
Co(4'-MeL)(5'-ClL)	0.081 V
$Co(5'\text{-}ClL)_2$	0.235 V
$Co(5'\text{-}NO_2L)_2$	0.589 V

[a]Potentials were measured in DMF and are reported vs. NHE.

Figure 4. Half wave potentials vs. σ_p for mononuclear Co(II) complexes containing various substituents on the isoindoline ligand.


Co (5′-NO2 L)2
Co (5′-Cl L)2
Co(4′-MeL)(5′-Cl L)
CoL2
Co (4′-MeL)2
0.6
0.4
0.2
0.0
Ef
-0.2
0.0
0.2
0.4
0.6
σ

EXPERIMENTAL SECTION

Synthesis. All organic ligands gave satisfactory carbon, hydrogen and nitrogen analyses, while metal complexes gave satisfactory carbon, hydrogen, nitrogen, and metal analyses.

Mononuclear Chelating Ligands, RLH. The synthesis and physical and spectral data for all the mononuclear chelating isoindoline ligands, RLH, employed in this study were reported earlier.[5]

Binucleating Ligands. All of the binucleating ligands reported in Table I were prepared by the general procedure illustrated below for the 4'-sec-butylpyridyl derivative 2g. Ligands with significantly lower solubility were purified by recrystallization from nitrobenzene or quinoline.

1,3,5,7-Tetra(2-(4-sec-butylpyridyl)imino)benzodipyrrole (2g). A 1L roundbottom flask was charged with 5.81 g (0.033 mol) of 1,2,4,5-tetracyanobenzene, 22.5 g (0.15 mol) of 2-amino-4-sec-butylpyridine,[5] 2.61 g of anhydrous calcium chloride, and 500 mL of methanol. The mixture was stirred at ambient temperature for 7 days and then warmed gradually to reflux temperature. After 2 days at reflux, the methanol was allowed to distill off and the solvent volume was maintained by the gradual addition of n-butyl alcohol. The suspension in butyl alcohol was heated at reflux for an additional 7 days. The mixture was allowed to cool and then filtered. The green crystalline solid was washed with methanol and dried in vacuo to a weight of 21.35 g. The crude solid was dissolved in methylene chloride, treated with activated charcoal, Norit A, overnight, and passed through a

column of celite (top) and silica gel (bottom). After the volume of eluate was reduced, 17.10 g of yellow crystalline product, 369-71°C, was obtained. With further volume reduction and addition of hexane, an additional 1.70 g of less pure ligand was also obtained for a yield of 76%.

NMR analysis of the product gave the following peaks: sec-butyl protons - 0.90 (t), 1.31 (d), 1.65 (quintet), 2.64 (sextet); pyridine protons - 6.92 (d), 7.31 (s), 8.5 (d); benzene protons - 8.77 (s); pyrrole protons - 14.08 (br, s).

Template Synthesis of the Binucleating Ligand (2). A mixture of 89 mg (0.5 mmol) of 1,2,4,5-tetracyanobenzene, 330 mg (2.2 mmol) of 2-amino-4-sec-butylpyridine, 200 mg (1.0 mmol) of cupric acetate hydrate, and 10 mL methanol was stirred at ambient temperature for 5 days followed by 3 days at reflux. After the solution was cooled, the solvent was allowed to evaporate and the residue was washed with water and dried to afford 430 mg of green powder. To this was added 5 mmol of KCN (325 mg), 20 mL of ethanol, and 10 mL of chloroform. Gentle heating, below the reflux temperature, was applied for 2 days. Upon being cooled, the green suspension was filtered and the insoluble material washed with chloroform. The combined filtrate washes were evaporated to dryness and the residue extracted with chloroform. The chloroform extract was passed through a minicolumn of alumina which removed most of the green pigment. From the eluant, a 45% yield (167 mg) of greenish yellow crystals was obtained which were identical spectroscopically to the ligand obtained via the $CaCl_2$-catalyzed route.

Solubility of Binucleating Ligands. An excess of binucleating ligand was added to 25 mL of benzene and warmed gently. The supersaturated solutions were allowed to stand at ambient temperature (23 ± 0.5°C) for at least 1 week before analysis. Aliquots were removed periodically, passed through a filter (Millipore LS, 5.0 μM), and, after appropriate dilution, were analyzed spectrophotometrically on a Cary 17D spectrophotometer. Using previously determined molar extinction coefficients, concentrations were calculated. Analyses were repeated periodically until concentrations had stabilized; relative solubility values are reported in Table I.

Preparation of (Acetato)[1,3-bis(2-pyridylimino)isoindolinato]-metal(II) Complexes [M(RL)OAc]. The following method was employed for the preparation of M(RL)OAc complexes of divalent Mn, Fe, Co, Ni, Cu, and Zn. The preparation of the Mn(II), Fe(II), and Co(II) complexes was carried out under an argon atmosphere; no effort was made to exclude air from the other preparations. One millimole of chelating ligand and 2 mmol of metal(II) acetate hydrate in 15 mL of methanol was stirred at ambient temperature for 24 h. After this time the suspension was filtered and the solid washed with methanol and dried in vacuo. Yields of complexes were generally 90% or higher. The colors of the M(4′-MeL)OAc complexes are as follows: Mn(II) tan, Fe(II) green, Co(II) gold-tan, Ni(II) green, Cu(II) brown, and Zn(II) yellow.

Preparation of Fe(4′-MeLH)Br_2. Under a helium atmosphere, a solution of 2.0 g (6.1 mmol) of 4′-MeLH in 40 mL of warm methanol was added to a solution of 2.6 g (9.0 mmol) of $FeBr_2 \cdot 4H_2O$ in 10 mL of

methanol. The reaction mixture was heated with stirring for 10 min. After the mixture was cooled to ambient temperature, 20 mL of diethyl ether was added to the mixture and stirred for 5 min. The green crystalline product (65% yield) was collected by vacuum filtration, washed with diethyl ether, and dried under a stream of helium.

Preparation of Mononuclear Metal(II) Complexes, $M(RL)_2$. The following general procedure was used to prepare mononuclear complexes of Mn(II), Fe(II), Co(II), Ni(II) and Zn(II) with RL = 4'-MeL. Preparations of iron and cobalt complexes were conducted in an inert atmosphere.

A solution of 0.7 mmole of the metal(II) perchlorate in 5 mL of methanol was added to a solution containing the mononucleating ligand (1.5 mmoles) and 0.5 mL of triethylamine in 40 mL of hot methanol. The reaction was heated at reflux for 30 min during which time a dark microcrystalline solid had formed. After being cooled, the mixture was filtered and the product was washed with hot methanol. The complexes CoL_2 and Co(5'-NO_2L), were prepared in the same fashion. The yields were: Mn(4'-MeL)$_2$ 74%, Fe(4'-MeL)$_2$ 77%, Co(4'-MeL)$_2$ 79%, Ni(4'-MeL)$_2$ 75%, Zn(4'-MeL)$_2$ 83%, CoL_2 91%, and Co(5'-NO_2L)$_2$ 12%.

Preparation of Bis(1,3-bis((5-chloro-2-pyridyl)imino)isoindolinato)cobalt(II). To 368 mg (1.0 mmol) of ligand and 119 mg (0.5 mmol) of cobaltous chloride hexahydrate under argon was added 10 mL of methanol and 1 mL of triethylamine. After being stirred for 16 h at 25°C, the mixture was filtered in the air and the product was

washed with methanol and dried in vacuo. A 97% yield (383 mg) of red-brown microcrystals was obtained, m.p. > 350° C.

Preparation of Bis(1,3-bis((4-sec-butyl-2-pyridyl)imino)isoindolinato)copper(II) [Cu(4'-sec-butylL)$_2$]. A solution of 34 mg (0.25 mmol) of anhydrous cupric chloride in 10 mL of methanol was added to 210 mg (0.51 mmol) of the chelating ligand, 4'-sec-butylLH, and stirred at ambient temperature.[7] The initial green solution changed to a yellow-brown suspension after a few minutes. After 15 min, 0.2 mL of triethylamine was added and the stirring was continued. After 45 min the suspension was filtered and the solid was washed with methanol and dried in vacuo. An 84% yield (186 mg) of gold microcrystals was obtained, mp 263-264.5°C.

Conversion of Co(4'-MeL)OAc to Co(4'-MeL)$_2$. A Schlenk tube was charged with 110 mg (0.25 mmol) of Co(4'-MeL)OAc, 88 mg (0.27 mmol) of chelating ligand, and 5 mL of pyridine. The dark red solution was stirred under argon at ambient temperature for 24 h. Water (4 × 5 mL) was added, and the resulting precipitate was collected, washed with water, and dried in vacuo to afford a quantitative yield of red-brown crystalline Co(4'-MeL)$_2$, mp 337-8° C.

Preparation of [1,3-bis((4-methyl-2-pyridyl)imino)isoindolinato]-[1,3-bis((5-chloro-2-pyridyl)imino)isoindolinato]cobalt(II) [Co(4'-MeL)(5'-ClL)]. To 184 mg (0.5 mmol) of 5'-ClLH and 222 mg (0.5 mmol) of Co(4'-MeL)OAc in a Schlenk tube under argon was added 10 mL of methanol and 1 mL of triethylamine. The mixture was stirred at ambient temperature for 2 days and then filtered in the air. The solid

was washed with methanol and dried in vacuo to afford a 92% yield (348 mg) of brown microcrystalline powder.

Preparation of Bis(1,3-bis((4-methyl-2-pyridyl)imino)isoindolinato)cobalt(III) Hexafluorophosphate [$Co(4'\text{-}MeL)_2PF_6$]. To 71 mg (0.1 mmol) of $Co(4'\text{-}MeL)_2$ and 57 mg (0.104 mmol) of ceric ammonium nitrate, $(NH_4)_2Ce(NO_3)_6$, in a Schlenk tube under argon was added 5 mL of methanol. After a few minutes a clear red-brown solution was obtained. After stirring at ambient temperature for 16 h, the solution was transferred to an open beaker and the solvent was allowed to evaporate. The solid residue was washed with water. Methanol (5 mL) and 25 mg (0.15 mmol) of NH_4PF_6 were added to the residue and the mixture was stirred until the solvent had evaporated. The residue was extracted with methylene chloride, and heptane was added in small amounts to the filtered extract. On standing dark crystals of the hexafluorophosphate salt were obtained as the methylene chloride solvate, $Co(4'\text{-}MeL)_2PF_6 \cdot 2CH_2Cl_2$, mp 256.5-257.5°C, 89% yield.

Anal: Calcd for: $C_{42}H_{36}N_{10}CoCl_2PF_6$: C, 49.14; H, 3.53; N, 13.65; Cl, 13.82; P, 3.02. Found: C, 49.5; H, 3.45; N, 13.7; Cl, 13,75; P, 3.0.

Preparation of Bis(1,3-bis((4-methyl-2-pyridyl)imino)isoindolinato)cobalt(III) Tetraphenylborate [$Co(4'\text{-}MeL)_2(Ph_4B)$]. A mixture of 44 mg (0.1 mmol) of Co(4'-MeL)OAc, 36 mg (0.11 mmol) of chelating ligand, 4'-MeLH, 41 mg (0.12 mmol) of sodium tetraphenylboron, and 6 mL of methanol was stirred for 24 h under argon

at ambient temperature. Then 77 mg (0.14 mmol) of ceric ammonium nitrate was added and the red-brown solution immediately changed to a brown suspension. After an additional 5 h at 25°C, the suspension was filtered in the air and the solid was washed with methanol and with water. After drying in vacuo, an 84% yield (87 mg) of gold-brown microcrystals was obtained.

Metal Exchange Studies. (a) Ni(4′-MeL)OAc and $Cu(OAc)_2 \cdot H_2O$. To 55 mg (0.125 mmol) of Ni(4′-MeL)OAc and 250 mg (1.25 mmol) of cupric acetate hydrate was added 3 mL of chloroform and 2 mL of methanol. After a few minutes a clear dark green solution was obtained and was stirred at ambient temperature for 24 h. The solvent was then allowed to evaporate, and the residue was washed with water and dried. The solid was extracted with methylene chloride and heptane was added in small aliquots to the extract. On standing, beautiful brown needles deposited. The crystals were collected, washed with heptane and ether, and dried to afford an 88% yield of Cu(4′-MeL)OAc.

(b) $Ni(4'\text{-MeL})_2$ and $Cu(OAc)_2 \cdot H_2O$. To 71 mg (0.1 mmol) of $Ni(4'\text{-MeL})_2$ and 200 mg (1.0 mmol) of cupric acetate hydrate was added 3 mL of chloroform and 2 mL of methanol. The resulting dark green solution was stirred at ambient temperature for 24 h and then evaporated under a stream of argon. The residue was extracted with methylene chloride and the solvent removed from the extract. The extract residue was extracted with benzene. From the benzene extract, 100 mg of green powder was obtained. The IR (KBr) spectrum was

identical to that of Cu(4'-MeL)OAc. Analysis by thin layer chromatography (SiO_2, EtOAc) of the powder showed no remaining $Ni(4'\text{-MeL})_2$. The yield of Cu(4'-MeL)OAc was 93%.

(c) $[Co(4'\text{-MeL})_2]PF_6$ and $Cu(OAc)_2 \cdot H_2O$. A solution of 86 mg (0.1 mmol) of $[Co(4'\text{-MeL})_2]PF_6$ and 200 mg (1.0 mmol) of $Cu(OAc)_2 \cdot H_2O$ in 3 mL of chloroform and 2 mL of methanol was stirred at ambient temperature for 24 h. The solvent was evaporated under a stream of argon and the residue was extracted with methylene chloride. After the methylene chloride was evaporated from the extract, the new residue was extracted with tetrahydrofuran. After addition of heptane to the tetrahydrofuran extract, dark crystals gradually deposited. The crystals (86 mg) were collected and dried in vacuo. The IR (KBr) spectrum was identical to that of the starting material. Thin layer chromatographic analysis (SiO_2; $CHCl_3$:EtOH, 10:1) of the product showed the absence of any Cu(4'-MeL)OAc, the potential exchange product.

Preparation of (AcO)ML-LM(OAc) (3). The general procedure for the preparation of (AcO)ML-LM(OAc) complexes (3) is illustrated below for the binuclear Cu(II) complex. The preparation of the Mn(II), Fe(II) and Co(II) complexes was carried out under an inert atmosphere.

To 745 mg (1.0 mmol) of binucleating ligand, HL-LH, and 1 g (5.0 mmol) of cupric acetate hydrate was added 50 mL of methanol, followed by 10 mL of chloroform. The suspension was stirred at ambient temperature for 72 h. The suspension was filtered and the solid was washed repeatedly with methanol until the washes were no

longer green. After drying in vacuo, a 97% yield (959 mg) of greenish yellow powder was obtained.

Preparation of LML-LML (4). Binuclear complexes of Mn(II), Co(II) and NI(II) were prepared by two different methods. The two different preparations are illustrated below for Co(II).

Preparation of (4'-MeL)CoL-LCo(4'-MeL). To 89 mg (0.2 mmol) of Co(4'-MeL)OAc, 74 mg (0.1 mmol) of HL-LH, and 5 mL of methanol in a Schlenk tube under argon was added 0.5 mL of triethylamine. After the dark brown suspension was stirred at ambient temperature for 20 h, an additional 10 mL of methanol was added. The suspension was filtered in the air and the solid was washed with methanol and dried in vacuo to afford a 91% (137 mg) yield of red-brown powder which exhibited a single spot on thin layer chromatography (SiO_2, EtOAc).

The Co(II) binuclear complex gave a ^1H NMR spectrum in $CDCl_3$ with the following peaks (vs. TMS at 34°C): aromatic protons: 48.6, 45.7, 37.0, 30.6, 29.1, and 27.5; sec-butyl protons: -4.3 and -7.6; and methyl protons: -13.7.

Alternate Preparation of (4'-MeL)CoL-LCo(4'-MeL). A Schlenk tube was charged with 98 mg (0.1 mmol) of (AcO)CoL-LCo(OAc), 65 mg (0.2 mmol) of 4'-MeLH, and 5 mL of methanol; the mixture was stirred under argon at ambient temperature. After 15 min, 0.5 mL of triethylamine was added to the brown suspension and the stirring was continued for an additional 16 h. An additional 10 mL of methanol was added and the supension was filtered in the air. The dark brown powder was washed with methanol and dried in vacuo to afford a 77%

yield (116 mg). The IR (KBr) spectrum was identical to that of material prepared by the first method.

Preparation of (4'-MeL)FeL-LFe(4'-MeL). Under a helium atmosphere, 160 mg (0.79 mmol) of $AgClO_4$ was added to a slurry of 430 mg (0.79 mmol) of Fe(4'-MeLH)Br_2 in 35 mL of methanol. After stirring briefly, the mixture was filtered to remove precipitated silver bromide. Toluene (15 mL) and a solution of 43 mg (0.79 mmol) of sodium methoxide in 20 mL of methanol were added to the filtrate resulting in a green to reddish brown color change. To this solution was added slowly a solution of 200 mg (0.27 mmol) of HL-LH and 29 mg of (0.54 mmol) sodium methoxide in 5 mL of methanol and 15 mL of toluene. After stirring for 1 h, the dark green solid was collected by vacuum filtration, washed with several portions of methanol, and dried under a stream of helium; 79% yield.

Preparation of [(4'-MeL)CoL-LCo(4'-MeL)]$(PF_6)_2$. To a suspension of 45 mg (0.03 mmol) of (4'-MeL)CoL-LCo(4'-MeL) in 5 mL of methanol was added sufficient methylene chloride to produce a homogeneous solution. To this solution was added 33 mg (0.06 mmol) of ceric ammonium nitrate, and the mixture was stirred for 0.5 h at ambient temperature after which time the solvent was evaporated under a stream of argon. The residue was washed with water, dried in vacuo, and then extracted with methylene chloride. To the CH_2Cl_2 extract was added 11 mg (0.07 mmol) of NH_4PF_6 in 3 mL of methanol; after 0.5 h of stirring, the mixture was filtered to remove a small amount of brown precipitate and the solvent was evaporated under a stream of

argon. The residue was washed with water and dried in vacuo to afford 45 mg of brown powder. The powder was extracted with ethyl acetate, and heptane was added in small aliquots to the extract. On standing, dark brown microcrystals deposited. The crystals were collected, washed with toluene, and dried in vacuo to afford a 67% yield (26 mg) of $[(4'\text{-MeL})\text{CoL-LCo}(4'\text{-MeL})](PF_6)_2$.

Preparation of (4'-sec-butylL)NiL-LNi(4'-sec-butylL) and Molecular Weight Determination. To 245 mg (0.25 mmol) of (AcO)NiL-LNi(OAc) and 226 mg (0.55 mmol) of 4'-sec-butylLH was added 20 mL of chloroform and the resulting solution was stirred at ambient temperature for 72 h. Heptane was added in small amounts until crystals deposited. A 60% yield (250 mg) of dark red crystals was obtained.

The solution molecular weight determination in toluene was carried out on the red crystals by Dr. M. Zinbo of the Ford Scientific Research Labs, using a Hitachi-Perkin Elmer molecular weight apparatus. This vapor-phase osmometry method gave an observed value of 1699 compared with a calculated value of 1680.

Preparation of (4'-MeL)CuL-LCu(4'-MeL). To 33 mg (0.033 mmol) of (AcO)CuL-LCu(OAc) and 22 mg (0.066 mmol) of 4'-MeLH was added 5 mL of methanol and 0.2 mL of triethylamine. The resulting suspension was stirred at 25°C, as the color gradually changed from olive-green to yellow-gold. After 3 h the suspension was filtered and the solid was washed with methanol and dried in vacuo. A 48% yield (27 mg) of gold-colored powder was obtained; mp $>$ 390°C.

Attempted Preparation of (4'-MeL)ZnL-LZn(4'-MeL). To 450 mg (1 mmol) of Zn(4'-MeL)OAc and 272 mg of (0.5 mmol) of binucleating ligand, HL-LH, was added 200 mL of methanol and 20 mL of triethylamine; the resulting suspension was stirred at ambient temperature for 7 days. The reaction mixture was filtered, washed with methanol, and dried in vacuo to afford a 60% yield (458 mg) of yellow-orange microcrystalline powder; mp $>$ 390°C.

Carbon, hydrogen and nitrogen analysis of the product was satisfactory for the binuclear Zn(II) complex, however, the proton NMR spectrum of the product gave a mononucleating ligand to binucleating ligand ratio of less than 2:1 expected for a discrete binuclear complex. This suggests that the product isolated contains a higher order polymer.

Electrochemistry. Tetrabutylammonium perchlorate, TBAP (Southwestern Analytical Chemicals), was dried in vacuo before use. Spectroquality acetonitrile and N,N-dimethylformamide, distilled under reduced pressure over 4-Å molecular sieves, were used for electrochemical measurements.

A Princeton Applied Research Model 173 potentiostat galvanostat coupled with a Model 179 digital coulometer and a ramp generator of our own design were used for constant potential electrolysis and cyclic voltammetry. A storage oscilloscope and an X-Y recorder were used to display the results. A Princeton Applied Research 174A Polarographic Analyzer was used in conjunction with an X-Y recorder for differential pulse voltammetry.

Constant potential electrolyses were carried out in a three-compartment H cell. The cell consisted of 25 mL sample and auxiliary compartments separated by a small center compartment. Each compartment was separated by a medium porosity sintered glass frit. A platinum gauze was used as the working electrode for electrolyses.

Cyclic voltammetry and differential pulse voltammetry were carried out in a single compartment cell containing approximately 5 mL of solution. The working electrode was a platinum button electrode. For all electrochemical measurements the supporting electrolyte used was 0.1 M TBAP. The Ag/Ag^+ reference electrode consisted of a silver wire immersed in an acetonitrile solution containing 0.01 M $AgNO_3$ and 0.1 M TBAP. The Ag^+ solution and silver wire were contained in an 8 mm glass tube fitted on the bottom with a fine porosity sintered glass frit. The auxiliary electrode consisted of a coiled platinum wire. All measurements were made in a helium atmosphere.

Small amounts of ferrocene were added to electrochemical solutions as an internal standard. Potentials for the complexes were measured vs. ferrocene.[16] The formal potentials were then adjusted to potentials vs. NHE with the assumption of a value of +0.400 V for the ferricenium/ferrocene couple.

Formal reduction potentials, E^f, were measured by cyclic voltammetry using the formula $E^f = (E_{p_a} + E_{p_c})/2$. The potentials determined in this way are approximate in that the systems examined did not display strict reversibility and corrections were not made for diffusion coefficients. Reduction potentials measured by cyclic voltammetry and differential pulse voltammetry agreed to within ± 10 mV.

Physical Measurements. Magnetic susceptibility measurements were obtained on samples at the ambient temperature using a Cahn Instruments Faraday balance, with $HgCo(SCN)_4$ as a calibrant. Diamagnetic corrections were made using Pascal's constants.

Proton NMR spectra were obtained on Varian EM-390 and JEOL FX90Q NMR spectrometers with $CDCl_3$ as the solvent and tetramethylsilane as a reference.

Electronic spectra were recorded on a Cary 14 spectrophotometer. Solution spectra were obtained using one centimeter matched quartz cells.

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3. Mononucleating ligands, 1, will be denoted as RLH; substituents on the pyridine ring precede the abbreviation, e.g., 4'-MeLH, where the prime designates the position of the pyridine ring. Mononuclear metal complexes are of two types: complexes with metal to ligand ratio of 1:1, ML(OAc), where L is the anion of the ligand LH and OAc also is bound to the metal, and complexes with metal to ligand ratio 1:2, ML_2, with two anionic tridentate ligands. HL-LH denotes the binucleating ligand, 2, with 4'-sec-butyl groups on the pyridine rings. Binuclear complexes containing the dianion of the ligand are denoted (OAc)ML-LM(OAc) or (4'-MeL)ML-LM(4'-MeL) depending on the other ligands bound to the metals.

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7. The Cu(II) complex, $Cu(4'\text{-MeL})_2$, is considerably more soluble in organic solvents than other $M(4'\text{-MeL})_2$ complexes. Solid samples of $Cu(4'\text{-MeL})_2$ usually contained small amounts of the ligand, 4'-MeLH, because the solubility of the ligand was similar

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to that of the metal complex. For this reason, the more soluble sec-butyl substituted ligand, 4'-sec-butylLH, was used in order to avoid coprecipitation of the Cu(II) complex and unreacted ligand.

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APPENDIX 2

Synthesis, Characterization, and Dioxygen Reactivity Studies of Mononuclear and Binuclear Iron Complexes of 1,3-Bis(2-pyridylimino)isoindolines

Synthesis, Characterization, and Dioxygen Reactivity Studies of Mononuclear and Binuclear Iron Complexes of 1,3-Bis(2-pyridylimino)isoindolines

INTRODUCTION

Reactions in which two or more electrons are transferred from a metal complex to a small molecular substrate are of considerable interest. Such multielectron reactions are potentially useful in chemical synthesis, solar energy conversion, and fuel cells. One reason for studying binuclear complexes of a binucleating analog of 1,3-bis(2-pyridylimino)isoindoline was their potential use as multielectron reactants.

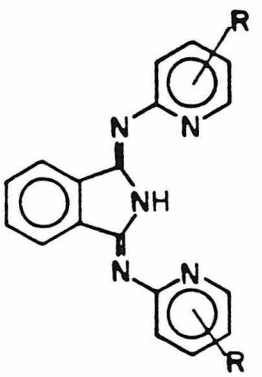
In preparing and characterizing mononuclear and binuclear complexes of 1,3-bis(2-pyridylimino)isoindolines, it was observed that preparations of a binuclear Fe(II) complex appeared to react with dioxygen.[1] Evidence for such reactivity was a distinct color change by solutions of the complex (N,N-dimethylformamide (DMF) or dichloromethane/methanol) upon exposure to dioxygen. Under similar conditions, the analogous Fe(II) mononuclear complex was unreactive. Additionally, related mononuclear and binuclear complexes of other transition metals were unreactive towards dioxygen. Although dioxygen reactivity of the binuclear Fe(II) complex was seemingly anomalous with respect to the behavior of related complexes, further investigation was warranted because of the possibility that the reaction involved multielectron transfer.

As a result of this investigation, it was determined that the

original preparations of the binuclear Fe(II) complex were not sufficiently pure for reliable dioxygen reactivity studies. An alternative preparation was developed by which analytically pure samples of the complex could be prepared. Synthesis, magnetic susceptibility, and electrochemical behavior of this complex have been reported previously.[2] Some additional characterization is reported here as well as syntheses and characterization of several unreported mononuclear and binuclear iron complexes of 1,3-bis(2-pyridylimino)isoindolines. Experiments were conducted to examine the dioxygen reactivity of solutions of analytically pure samples of the binuclear Fe(II) complex. No evidence for such reactivity was observed. Experimental details and a discussion of the results are also reported here.

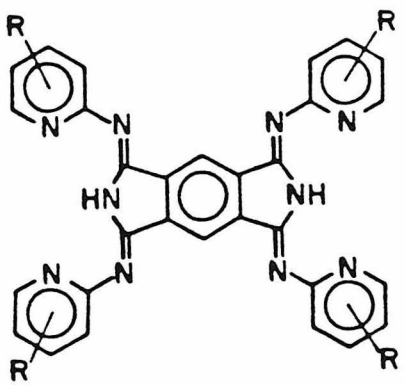
RESULTS AND DISCUSSION

Synthesis and Characterization. The binuclear Fe(II) complex which was purported to react with dioxygen incorporates both mononucleating and binucleating 1,3-bis(2-pyridylimino)isoindoline ligands, 1 and 2. The original samples of this complex,



1

4′-MeLH,[3] R = 4-CH_3



2

HL-LH,[3] R = 4′-sec-butyl

(4′-MeL)FeL-LFe(4′-MeL), were prepared by the reaction of HL-LH with 2 equiv of Fe(4′-MeL)(OAc)[2] under basic conditions (eq 1).

$$\text{HL-LH} + 2[\,\text{Fe(4′-MeL)(OAc)}\,] \xrightarrow{\text{base}} \text{(4′-MeL)FeL-LFe(4′MeL)} + 2H^+ \quad (1)$$

Magnetic susceptibility measurements yielded values significantly lower than the expected value of 5.12 B.M.[2] Additionally, microanalytical data for these samples were not in agreement with the

calculated values for (4′-MeL)FeL-LFe(4′-MeL). Instead, the best fit for the data was a mixture of (4′-MeL)FeL-LFe(4′-MeL), Fe(4′-MeL)(OAc), and HL-LH. Because these experimental data were indicative of a product of unacceptable purity, an alternative synthetic approach was developed.

The complex, (4′-MeL)FeL-LFe(4′-MeL), was successfully prepared by the reaction of HL-LH with 2 equiv of $Fe(4'\text{-MeLH})Br_2$ which was first dehalogenated with Ag^+ (eq 2 and 3).[2] For products of

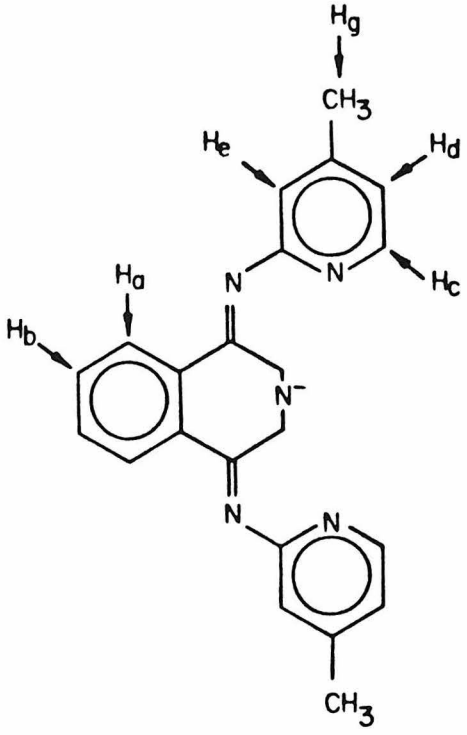
$$[Fe(4'\text{-MeLH})Br_2] + Ag^+ \rightarrow [Fe(4'\text{-MeLH})Br] + AgBr \qquad (2)$$

$$HL\text{-}LH + 2[Fe(4'\text{-MeLH})Br] + 4NaOCH_3 \rightarrow$$
$$(4'\text{-MeL})FeL\text{-}LFe(4'\text{-MeL}) + 4CH_3OH + 4Na^+ + 2Br^- \qquad (3)$$

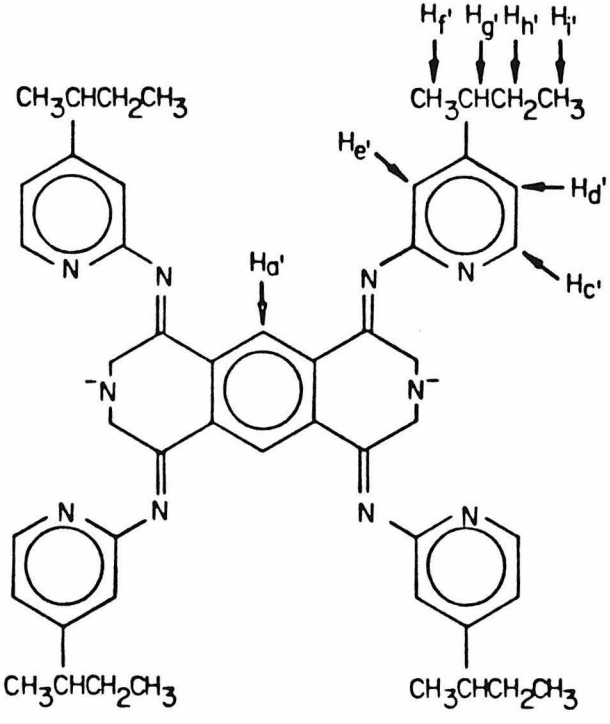
this reaction, the average μ_{eff}(298 K)/Fe(II) value, 5.13 B.M., and microanalytical data are within experimental error of the expected values. Additionally, the ^1H NMR spectrum (Table I and Figure 1) is consistent with the expected formulation. Specifically, the 3:1 ratio of methyl protons (H_g) to the methine protons (H_g') establishes that the complex is a discrete binuclear species. A lower ratio would be indicative of polynuclear contamination.

The binuclear Fe(II) complex, (4′-MeL)FeL-LFe(4′-MeL) was oxidized with 2 equiv of ferricenium tetrafluoroborate ($(Cp_2Fe)BF_4$) in methylene chloride, with the corresponding binuclear Fe(III) complex being isolated as a methylene chloride sesquisolvate of the bis-tetrafluroborate salt (eq 4). The same method was also used to oxidize $Fe(4'\text{-MeL})_2$ to $Fe(4'\text{-MeL})_2BF_4$ (4). Both mononuclear and binuclear

Table I. Proton NMR Data for (4′-MeL)FeL-LFe(4′-MeL) in $CDCl_3$



4′-MeL



L–L

Assignment	Chemical shift[a]
H_a	9.29
$H_{a'}$	9.99
H_b	11.31
H_c	NO[b]
$H_{c'}$	NO
H_d	32.80
$H_{d'}$	32.80
H_e	42.14
$H_{e'}$	42.14
$H_{f'}$	0.48
H_g	-25.33
$H_{g'}$	-7.54
$H_{h'}$	2.27
$H_{i'}$	0.48

[a]Values are given in ppm vs. Me_4Si.

[b]NO = not observed.

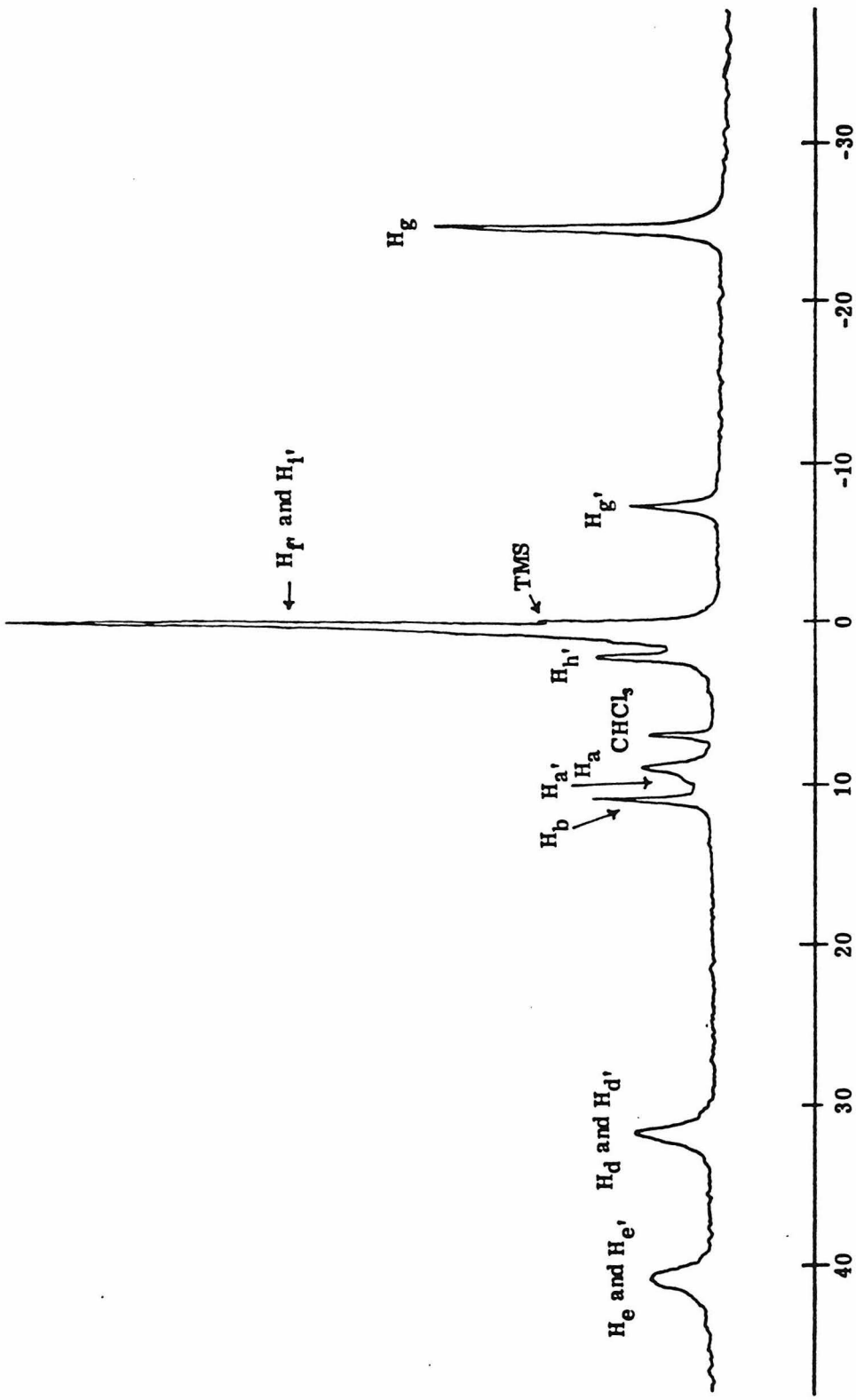


Figure 1. ^1H NMR spectrum of (4'-MeL)FeL-LFe(4'-MeL) in $CDCl_3$.

$$(4'\text{-MeL})\text{FeL-LFe}(4'\text{-MeL}) + 2(Cp_2Fe)BF_4 \xrightarrow{CH_2Cl_2}$$

$$[(4'\text{-MeL})\text{FeL-LFe}(4'\text{-MeL})](BF_4)_2 \cdot \tfrac{3}{2}CH_2Cl_2 + 2Cp_2Fe \qquad (4)$$

Fe(III) complexes are low spin with μ_{eff}(298 K)/Fe(III) values in the range of 2.1-2.3 B.M. In the ^{1}H NMR spectrum of Fe(4'-MeL)$_2$BF$_4$, three broad signals attributable to the complex and seven sharp signals characteristic of the free ligand, 4'-MeLH, are observed. This latter observation is suggestive of some ligand dissociation by the Fe(III) complex. The electrochemical behavior of freshly prepared DMF solutions of both the mononuclear and binuclear Fe(III) complexes was identical with that of the analogous Fe(II) complexes. However, over a period of $\sim$20 min, irreversible waves appeared in cyclic voltammetric scans of solutions of these complexes. This result also is suggestive of ligand dissociation with the irreversible waves being attributed to related complexes in which a 1,3-bis(2-pyridylimino)-isoindoline ligand has been replaced by solvent molecules.

A third Fe(III) complex, Fe(4'-MeL)Cl$_2$ (5), was prepared and isolated from a reaction of 4'-MeLH with FeCl$_3$ (eq 5). In the infrared

$$FeCl_3 + 4'\text{-MeLH} \rightarrow \text{Fe}(4'\text{-MeL})Cl_2 + HCl \qquad (5)$$

spectrum of this complex, two equal intensity absorptions are observed at 348 and 363 cm^{-1}. These absorptions are attributed to Fe(III)-Cl stretching;[4] with two such absorptions being expected for a complex with C_{2v} symmetry.[5] This Fe(III) complex is high spin with a μ_{eff}(298 K)/Fe(III) value equal to the expected spin-only value, 5.92 B.M. There are four extremely broad signals in the ^{1}H NMR

spectrum of this complex; only the methyl protons at 9.52 ppm could be definitively assigned.

Dioxygen Reactivity Studies. Solutions of (4'-MeL)FeL-LFe(4'-MeL) (~1 mM) in methylene chloride, 1:1 methylene chloride/methanol, and DMF exposed to dioxygen for 1 week showed no reactivity by electronic absorption spectroscopy. The intensity of the absorption at 755 nm (ϵ = 1450) decreased only slightly, and the appearance of an absorption at 843 nm (ϵ = 1220) characteristic of the expected oxidized product, (4'-MeL)FeL-LFe(4'-MeL)$^{2+}$, was not observed. Solutions of Fe(4'-MeL)$_2$ behaved similarly. The analogous Co(II) and Ru(II) binuclear complexes, with M(III)/M(II) reduction potentials similar to that of the Fe(II) binuclear complex,[2,6] also were unreactive towards dioxygen in aprotic or weakly protic solvents.[1]

In such solvents with very low proton concentrations, this lack of multielectron dioxygen reactivity is not completely surprising, since the formation of free O_2^{2-} is thermodynamically unfavorable. Only if O_2^{2-} is somehow stabilized by an interaction with the complex would there be a driving force for this reaction in aprotic or weakly protic solvents. Thermodynamically more favorable conditions for the two-electron reduction of dioxygen would be provided by acidic media. However, since the binuclear Fe(II) complex decomposes under these conditions, dioxygen reactivity of this complex in thermodynamically favorable media could not be studied. The related Ru(II) binuclear complex, (4'-MeL)RuL-LRu(4'-MeL),[6] which is not decomposed in acidic media, showed no dioxygen reactivity in aqueous hydrochloric acid solutions.[1]

The original samples of (4'-MeL)FeL+LFe(4'-MeL) for which O_2 reactivity was observed most likely contained significant quantities of unreacted starting materials, HL-LH and Fe(4'-MeL)(OAc) (vide supra). This latter species, a five-coordinate mononuclear Fe(II) complex, does react with dioxygen in solution. It is likely that the apparent reactivity of the original samples of (4'-MeL)FeL-LFe(4'-MeL) was due to Fe(4'-MeL)(OAc) which was a significant component of these samples.

EXPERIMENTAL SECTION

General Considerations. Unless noted otherwise, solvents were reagent grade and were used without further purification. Methylene chloride was distilled from calcium hydride and diethyl ether was distilled from sodium. The ligand, 4′-MeLH,[7] and the complexes, $Fe(4'\text{-}MeL)_2$ and (4′-MeL)FeL-LFe(4′-MeL),[2] were prepared by published methods. Microanalytical data are reported here for the latter complex: Anal. Calcd. for $C_{86}H_{82}Fe_2N_{20}$: C, 68.52; H, 5.48; N, 18.58; Fe, 7.41. Found: C, 68.58; H, 5.52; N, 18.52; Fe, 7.2.

Physical Measurements. Magnetic susceptibility measurements were obtained at ambient temperature using a Cahn Instruments Faraday balance. The balance was calibrated using $HgCo(SCN)_4$ and diamagnetic corrections were made using Pascal's constants.[8] Infrared spectra were recorded on a Beckman 4140 spectrometer. Samples were examined as KBr pellets. ^1H NMR spectra were recorded on a JEOL FX90Q spectrometer with $CDCl_3$ as the solvent and Me_4Si as an internal reference. Electrochemical procedures have been described previously.[2] Electronic absorption spectra were recorded on a Cary 14 spectrophotometer using matched quartz 1-cm cells. Elemental analyses were determined by the California Institute of Technology's analytical facility.

[(4′-MeL)FeL-LFe(4′-MeL)]$(BF_4)_2 \cdot \frac{3}{2}CH_2Cl$ (3). All manipulations in this synthesis were carried out using high-vacuum line techniques. A solution of 50 mg (0.033 mmol) of (4′-MeL)FeL-LFe(4′-MeL) and 18 mg (0.066 mmol) of ferricenium tetrafluoroborate[9] in 20 mL of CH_2Cl_2 was stirred for 5 min. After carefully removing all but 3 mL

of the solvent, diethyl ether was slowly distilled into the reaction flask until a reddish solid just began to precipitate. The mixture was then quickly filtered. Deep red 3 (29 mg, 49%) was crystallized from the filtrate, washed with diethyl ether, and dried in vacuo. Anal. Calcd. for $C_{87.5}H_{85}B_2Cl_3F_8Fe_2N_{20}$: C, 58.11; H, 4.73; N, 15.49; Fe, 6.17. Found: C, 57.76; H, 4.88; N, 15.54; Fe, 6.3.

[Fe(4′-MeL)$_2$]BF$_4$ (4). All manipulations in this synthesis were carried out using high-vacuum line techniques. A solution of 198 mg (0.28 mmol) of Fe(4′-MeL)$_2$ and 77 mg (0.28 mmol) of ferricenium tetrafluoroborate in 30 mL of CH_2Cl_2 was stirred for 5 min. All but 4 mL of the solvent was removed and 20 mL of diethyl ether was distilled into the reaction flask. Dark red 4 (131 mg, 59%) was crystallized from this solution, washed with diethyl ether, and dried in vacuo. Anal. Calcd. for $C_{40}H_{32}BF_4FeN_{10}$: C, 60.40; H, 3.98; N, 17.61; Fe, 7.02. Found: C, 59.47; H, 3.91; N, 17.48; Fe, 7.0.

Fe(4′-MeL)Cl$_2$ (5). A solution of 490 mg (1.5 mmol) of 4′-MeLH in 30 mL of warm toluene was added dropwise to a filtered solution of 275 mg (1.7 mmol) of $FeCl_3$ in 40 mL of methanol. The resulting dark red solution was stirred and heated at reflux for 5 min. The volume of solution was then reduced to 40 mL by evaporating the solvent at boiling. Upon being cooled to ambient temperature, the solution yielded red-purple crystals of 5 (380 mg, 56%). The product was collected, washed with diethyl ether, and dried in vacuo. Anal. Calcd. for $C_{20}H_{16}Cl_{12}FeN_5$: C, 53.01; H, 3.56; N, 15.46. Found: C, 53.49; H, 3.65; N, 15.66.

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